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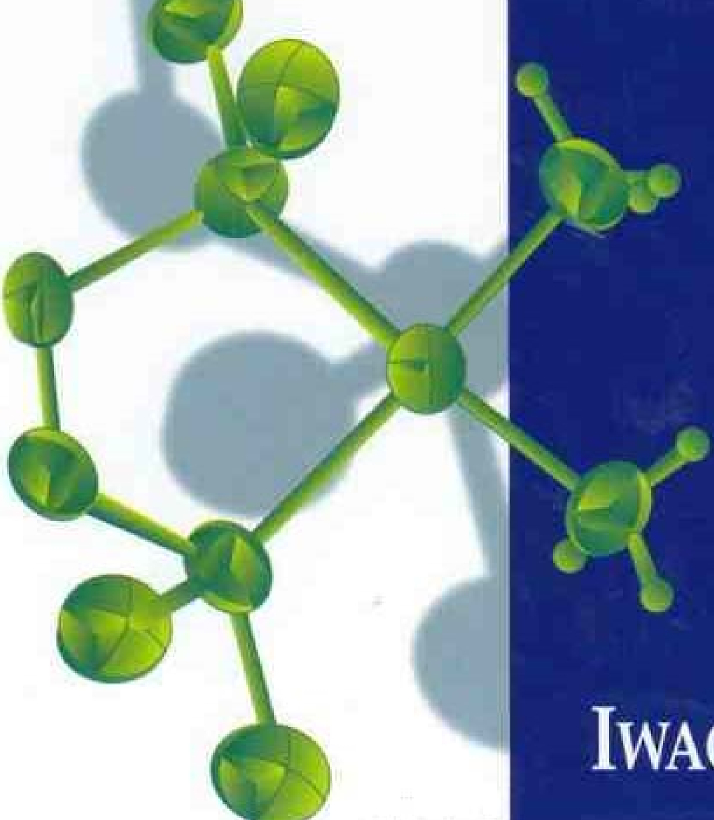

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Applications of Organometallic Compounds

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Contents

Preface

Organometallic compounds are used not only by organometallic chemists but also organic synthetic chemists, natural products synthetic chemists, pharmaceutical synthetic chemists and perfume synthetic chemists in synthetic reactions as catalysts or as reagents. As the properties of the organometallic compounds have gradually become apparent, many new synthetic methods using organometallic compounds have been discovered. In many cases, the desired compounds have been synthesized via many reaction steps, and the reactions involved two or more kinds of organometallic compounds or inorganic metallic compounds such as $PdCl2$ and $RhCl(PPh3)3$. Since the latter inorganic metallic compounds in most cases act as catalysts for the organometallic compounds having a metal-carbon bond in the course of the reaction, the reactions using these inorganic metallic compounds are thus also considered to the organometallic reactions.

Since there are many kinds of organometallic compounds and these have different properties, then we should first of all understand the properties of each organometallic compound before using these compounds in synthetic reactions. However, at present, even if a person decides to investigate these properties, there are few books dealing with these compounds.

This book was compiled by mainly putting together reviews on nine representative main group organometallic compounds and eleven transition metal organometallic compounds, and it includes their histories of utilization. These reviews have been published in *Kagaku Kogyo (Chemical Industry)* in the September 1990 to March 1996 issues. This book also includes more recent articles. To understand these organometallic compounds a comprehensive knowledge of metallic elements is required. Therefore this book is designed to show the properties of each metallic element. Side reactions caused by impurities in each organometallic reagent are often regarded as significant in synthetic reactions and probably many investigators have gone through many difficulties. This book shows the production process of each metal in order to give knowledge to the reader on the possible impurities on each metal.

This book is intended as an introduction for research chemists who want to understand the outline of each of the organometallic compounds, and hopefully is of value to undergraduate students, graduate students and research workers as well.

Finally, I should like to express my sincere gratitude to Dr. Sumio Chubachi for reading the full manuscript, which enhanced its accuracy and clarity, and for providing much valuable constructive criticism.

1 Introduction

Organometallic compounds are defined as those compounds having a M–C bond formed by a metal atom (M) bonding with a carbon atom (C). Even if the compounds have the M–C bond, the compounds are excluded from the group of organometallic compounds if they show apparently inorganic compound-like properties, e.g., metal carbides and metal cyanides. In contrast, even if the compounds do not have a M–C bond, they are treated as organometallic compounds if they show similar properties to organometallic compounds, e.g., metal hydrides and N_2 coordination complexes.

Inorganic compounds comprise of mostly three kinds, i.e., metals, ores and substances having strong ionic bond properties. Metal carbides also comprise three kinds of compounds, corresponding to the above. There are metal-like carbides (e.g., WC, TiC and TaC), diamond-like carbides (e.g., ZrC, VC, HfC and SiC) and salt-like carbides (e.g., CaC_2 and Be_2C). The melting point, density, electrical resistivity and microhardness of these metal carbides, metal cyanides and diamond are shown in Table 1.1 [1–4]. Even though SiC is a representative metal carbide, and is a compound having a metal–carbon bond, it has a higher temperature–resistance property than metallic materials and has been developed as a material for higher efficiency engines and turbines.

But organometallic compounds are generally very liable and their reactivities are high. Hence, organometallic compounds are largely utilized by taking advantage of their high reactivity. Furthermore, organometallic compounds contain many elements in the molecule unlike organic compounds. They are utilized for their wide range of properties since each element has its own properties.

Organometallic compounds are used in the following four categories in comparison with organic compounds and inorganic compounds.

The first is a higher reactivity and a high reaction selectivity. The high reactivity is the most representative property of organometallic compounds described above. On the other hand, as there are many kinds of metal elements, the reaction can be carried out in high selectivity by using the most suitable organometallic compounds capable of containing many elements. Organometallic compounds are actually used as various kinds of catalysts and as organosynthetic reagents by applying these characteristics. For example, the organoaluminum compounds and cyclopentadienyltitanium compounds of Ziegler–Natta catalysts, rhodiumcarbonyl compounds of Monsanto's acetic acid catalysts, etc. are available as catalysts. Grignard reagents, organolithium compounds, organoaluminum compounds, organozinc compounds and organoboron compounds are available as organosynthetic reagents.

Table 1.1 Physical properties of metal carbides and metal cyanides [1–4]

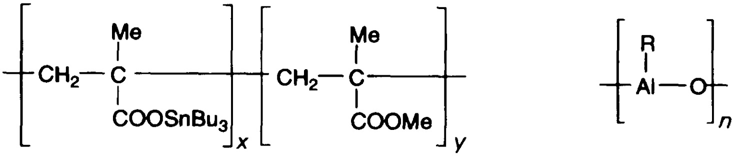
Compound	Melting point (°C)	Density (g/cm^3)	Electrical resistivity (mW cm)	Microhardness (kg/mm^2)
WC	2776	15.7	22	1200–2000
TiC	3067	4.93	68	≈3000
TaC	3985	14.48	25	1800
NbC	3610	7.78	35	2000
ZrC	3420	6.46	42	2700
HfC	3930	12.3	37	2600
VC	2650	5.36	60	2900
Cr_3C_2	1810	6.68	75	1400
Mo_2C	2520	9.18	71	1500
SiC	2300 dec	3.20	1000	2580
CaC_2	2300	2.34	—	—
Be_2C	2300	2.42	1000	2690
NaCN	562	1.60	—	—
KCN	634	1.55	—	—
C (diamond)	3800 dec	3.52	10^{18}	7600

The second is to have a wide range of characteristics since there are many kinds of metal elements. These organometallic compounds are available for many kinds of reagents. As well as the group 14 elements, Si, Ge, Sn and Pb are in the same group with C; therefore the organometallic compounds they form have highly covalent bond properties. Hence, these organometallic compounds generally form many stable compounds that are different from the other group of organometallic compounds. These compounds are not utilized for their high reactivities but they are utilized for other kinds of properties such as microbicidal, pesticidal, anticancer, octane number improving, water repellent, antifoaming and mold releasing properties. In particular, organosilicons have a wide range of uses as described later in Chapter 8.

The third is to easily isolate a pure metal or its metallic compound. Generally it is difficult to produce a highly pure metal directly from its ores and it is also not easy to isolate highly pure metallic compounds by the usual synthetic methods. However, it is not difficult to isolate the organometallic compounds containing only a single metal. Hence, it is easy to produce highly pure metal by the decomposition of organometallic compounds containing a simple metallic component. It is also easy to produce highly pure metallic compounds from this highly pure metal. These properties of organometallic compounds are also applied for the production of new ceramics [5–7]. As in the production of pure metals, these are actually produced by thermal decomposition of metal carbonyls. Pure metallic iron and nickel are available. First, $Fe(CO)_5$ or $Ni(CO)_4$ are prepared. Then each highly pure metal is produced by the thermal decomposition of these metal carbonyls. Highly pure metals or metal compounds are also produced by decomposition with light, a plasma and electron beam, etc. The process to produce highly pure objective chemical substances on the base plate is called CVD (Chemical Vapor Deposition Process). CVD with organometallic compounds as chemical substances is called MOCVD (Metal–Organic Chemical Vapor Deposition) or OMVPE (Organometallic Vapor Phase Epitaxy). Me_3Al, t-Bu_3Al, $Cr(CO)_6$, $(\eta^6\text{-}C_6H_6)_2Cr$, Cp_2Co, $CpCuPEt_3$, $Fe(CO)_5$, Cp_2Fe, Et_4Pb, $Mn_2(CO)_{10}$, $Ni(CO)_4$, Cp_2Ni, $(\eta^3\text{-}C_3H_5)_2Pd$, $Pt(CO)_2Cl_2$, CpRhCOD, $Ru_3(CO)_{12}$, Me_4Sn, $(neopentyl)_4Ti$ and Me_2Zn, etc. as the organometallic compounds are used [7]. These compounds are available for the production of semiconductor elements, electroconductive materials, magnetic materials, hard materials, heat-resistant materials, and superconductive materials, etc. For example, SnO_2 (a transparent electroconductive material) is produced by thermal decomposition of Me_4Sn with O_2. TiC (a hard material) is produced by thermal decomposition of $(neopentyl)_4Ti$ [5–7].

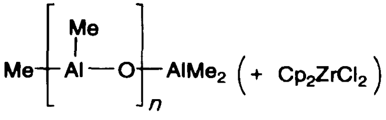
Ceramics are china, porcelain, glass, cement and the other fire-resistant materials obtained by treating natural substances at high temperatures. However, new ceramics are ceramics having various kinds of functions such as high electroconductive, photoconductive, dielectric, transparent, magnetic, highly heat resistant, highly strong, and piezoelectric properties. These are able to show higher functions when each component is of a higher purity. However, it is difficult to always get the substances having a constant composition from natural raw materials. So metal oxide, metal carbides, metal nitrides, metal borides and silicides, etc. are used as the raw materials for the new ceramics. Organometallic compounds are used for the raw materials of these highly functional new ceramics since these highly pure raw materials are easily prepared from organometallic compounds. Recently, organometallic compounds have increasingly been utilized as the raw materials for these wide variety of new ceramics [8].

The fourth is organometallic high polymers. The organometallic high polymers are used as the compounds having both properties of high polymers and organometallic compounds. For example, $(Bu_3Sn)_2O$ is an excellent additive for marine paints. The organotin polymer of this type of additive is shown in Figure 1.1. This polymer was used in quantities of 10 000 tons or more per year in the 1980s as an ablative self-polishing polymer. It was the best marine paint since it made the best use of polymer properties. Kaminsky's catalyst is a catalyst that was found in 1980 by Kaminsky. It consists of two components: one is a catalyst of a metalocene and another is an organoaluminum polymer prepared by hydrolysis of trimethylaluminum. It is also called a metalocene catalyst as shown in Figure 1.1 [9–19]. The Kaminsky catalyst came to public notice as the catalyst for the preparation of highly stereospecific syndiotactic polypropylene [10–13]. The most used organometallic compounds are organosilicon compounds, especially silicones. The silicones are organosilicon polymers that have a polysiloxane skeleton shown in $(Si(Me)_2{-}O{-})_n$. Their surface tensions are small since their intermolecular forces are small. They have a highly antifoaming property, mold release characteristics, water repellency, permeability to gases and lubricating properties, and furthermore



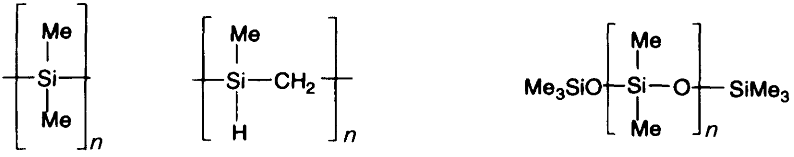
ablative self-polishing polymer

precursor of alumina



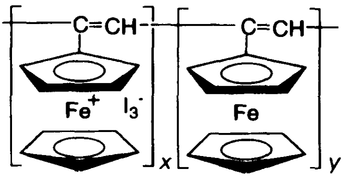
$n = 5-20$

Kaminsky catalyst



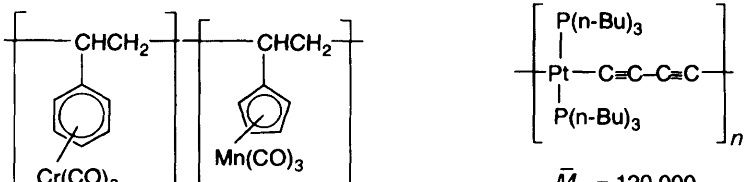
precursor of silicon carbade

silicone



$10^{-6} - 10^{-7}\ \Omega^{-1}\mathrm{cm}^{-1}$

polyethynylferrocene



$\bar{M}_w = 120{,}000$

polyvinylmetallocene copoymer

polyplatiniumdiyne

Figure 1.1. Some organometallic polymers [9–19].

they have a high resistance to heat, a resistance to oxidation, and electrical insulating properties, etc. Thus, the silicones are used as a wide range of materials.

Organometallic polymers have been studied in two types of compounds: the metal is in a principal chain or in a side chain. They have been developed as semiconductive materials, photoconductive materials, liquid crystals, superconductive materials, catalysts, etc.

The organometallic compounds are mainly used in the production of many kinds of fine chemicals in small quantities compared with organic compounds and inorganic compounds. Since the competition in development of each company is intense, the manufacturing processes and the amounts of production have almost never been published.

Furthermore, there are many compounds that each company produces and utilizes by itself since many compounds are liable. Thus it is difficult to obtain the data on the amounts of production and consumption of organometallic compounds. However, *Organometallics*, published in 1989, reported on the production of organometallic compounds as shown in Table 1.2 [20]. The organolead compounds in the second place are mainly tetraethyllead that is used as an octane number improver of gasoline, described later in Chapter 11. Tetraethyllead began to be regulated in its utilization by environmental problems in the 1970s, and was sharply cut in its utilization in developed countries in the 1990s. It is still being used in developing countries where these are relatively leniently regulated. MMT (methylcyclopentadienylmanganese tricarbonyl, $(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn(CO)}_3$) can be used as an octane number improver instead of tetraethyllead. By using MMT as an additive for gasoline NO_x emission is reduced by about 20 % compared with lead-free gasoline. Thus MMT is found to be an excellent additive for environmental problems. It has been used since 1977 in Canada, and in the United States it began to be used from the end of 1995.

On the production amounts of organometallic compounds given in *Marketing Research Report of Chemical Economic Handbook* by SRI Company in 1995, organotin compounds, organolithium compounds and organomagnesium compounds are 45 200 ton, 1500 ton and 800 ton per year, respectively. These values are higher than those in Table 1.1 published in 1989. But the amount of organoaluminum compounds in the SRI report is 23 100 ton, which is less than that in Table 1.1.

Table 1.2 Production figures of organometallic compounds [20]

Organometallic compound	Production (t/yr)
organosilicon compound (silicones)	700 000
organolead compound (Pb-alkyl)	600 000 (declining)
organoaluminium compound	50 000
organotin compound	35 000
organolithium compound	900

By taking into consideration recent development rates, it is difficult to consider that the actual production amounts are decreasing. It is supposed that one of these two results is questionable [21–23]. From these data, in the order on the production amount, the first is organosilicon compounds. However, it is not postive about whether the second place is occupied by organotin compounds, organoaluminum, organolead compounds or organomanganese compounds. Anyway, these organometallic compounds also play important parts for industrial chemistry and organosynthetic chemistry.

REFERENCES

[1] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol. A5, p. 61, 1986.
[2] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol. A8, p. 159, 1987.
[3] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 4th. Ed., John Wiley, vol. 4, p. 841, 1992.
[4] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 4th. Ed., John Wiley, vol. 7, p. 753, 1993.
[5] S. Fujita and S. Fujita, *Kino Zairyo*, March (1989) 5.
H.M. Manaservit, *Appl. Phys. Lett.*, **12** (1968) 156.
[6] M. Sato and M. Suzuki, *Kagaku Kogaku*, **51** (1987) 389.
[7] J.T. Spencer, *Prog. Inorg. Chem.*, **41** (1994) 145.
[8] New Ceramics, *Zairyo to sono Ooyo*, New Ceramics Konwakai, Nikkan Kogyo Shinbunsha, 1997.
[9] W. Kaminsky, *Adv. Organomet. Chem.*, **18** (1980) 99.
[10] R. Sugimoto, *Kagaku to Kogaku*, **46** (1993) 1097.
J.A. Ewen, R.L. Jones, A.R. Razavi and J.D. Ferrara, *J. Am. Chem. Soc.*, **110** (1988) 6255.
[11] K. Soga and T. Shiono, *Kagaku Kogyo*, **44** (1993) 505.
W.P. Long and D.S. Breslow, *J. Am. Chem. Soc.*, **82** (1960) 1953.
[12] K. Soga and T. Kahara, *Kagaku to Kogaku*, **46** (1995) 743.
[13] K. Mashima and A. Nakamura, *Shokubai*, **36** (1994) 572.
W. Kaminsky, H. Sinn, H.J. Vollmer and R. Woldt, *Angew. Chem. Int. Ed. Engl.*, **19** (1980) 390.
[14] *Yuki Kinzoku Polymer*, N. Hagiwara and M. Nakamura ed., Gakkai Shuppan Center 1982.
[15] *Muki Kobunshi I*, M. Kajiwara and K Murakami ed., Sangyo Tosho, 1992.
[16] K. Sonogashira, S. Takahashi and N. Hagihara, *Macromolecules*, **10** (1977) 879.
[17] S. Takahashi, E. Murata, K. Sonogashira and N. Hagihara, *J. Polymer Sci., Polymer Chem. Ed.*, **18** (1980) 661.
[18] C.U. Pittman, Jr. and Y. Sasaki, *Chem. Lett.*, (1975) 383.
[19] C.U. Pittman, Jr. P. L. Grube, O.E. Ayers, S.P. McManus, M.D. Rausch and G.A. Moser, *J. Polymer Sci. A-1*, **10** (1972) 379.
[20] C. Elschenbroich and A. Saltzer, *Organometallics*, VCH, Weinheim, p. 6, 1989.
[21] *SRI Chemical Economics Handbook Marketing Research Report, Organometallics*, 681.7000 A, Feb. 1995.

[22] *SRI Chemical Economics Handbook Marketing Research Report, Silicones*, 583.0100A, Jan. 1993.

[23] *SRI Chemical Economics Handbook Marketing Research Report, Gasoline Octane Improvers*, 543.7500A, May 1994.

2 History of Organometallic Chemistry

The history covering the whole area of organometallic chemistry will be described before describing each organometallic compound.

2.1 THE FIRST ORGANOMETALLIC COMPOUND

Some books [1–4] on organometallic chemistry described Zeise's salt [5] reported in 1827 or a cacodyl compound (tetramethyldiarsine) synthesized by Bunsen ten years later [6] as the first organometallic compound. However, the synthetic reaction of cacodyl compounds was reported in 1760 by Cadet at least 80 years before Bunsen's report [7,8]. Cadet obtained the cacodyl as liable substance which shows the characteristics of organometallic compound. However, in general, it is not considered as the first compound of the organometallic compound group since, it was not isolated as a single substance and its composition was not revealed.

Louis Clause Cadet de Gassicourt was a Parisian military apothecary. He was working on cobalt solutions for the purpose of using them as invisible inks. The two common ores of cobalt, smaltite (CoAs) and cobaltite ($CoAsS_2$), both contain arsenic, were treated with an acid solution, and arsenic trioxide (As_2O_3) was formed as a by-product. He carried out the following reaction with this oxide of the by-product [7–9]. A very fine powder of arsenic trioxide was added to the same amount of potassium acetate, and he heated them slowly. After some time, a faintly colored liquid, having an extremely penetrating odor of garlic, appeared. It was followed by a red-brown liquid which filled the flask with a thick vapor. The first liquid effervesced strongly in fixed alkaki, giving off an unbearably strong stench of garlic; even the strongest vinegar could not destroy the odors impregnated in these vessels; they only disappeared after several month's exposure to open air. The second red-brown liquid deposited, after a certain time, a beautiful yellow material that he suspected to be a metallic substance; when this material was precipitated, the liquid became clear and so light that it floated on the first liquid. These two liquids were very clear and had a faint amber color. If exposed to air, they fumed like phosphorus, they were slightly soluble in water and spontaneously ignited when poured from the receiver.

In 1760, it was the days of elements such as hydrogen, oxygen, chlorine and iodine, and compounds such as carbon dioxide were not known. Therefore, it may safely be said that it was impossible to clarify the components of Cadet's liquid in those days. Cadet's fuming arsenic liquid fascinated many chemists, and his work has been repeated. Early in the nineteenth century, it was found that CO_2 and hydrocarbons were involved during the distillation of Cadet's liquid, while As_2O_3 sublimed out and K_2CO_3 remained in the flask. The upper of the two liquids turned out to be merely a solution in water and acetic acid; it was the lower liquid that had the obnoxious odor and the flammability in air [10]. In 1837, Bunsen reported in detail on this Cadet's liquid [6]: three layers of products are found. At the bottom is a considerable quantity of reduced arsenic, and the middle layer is a brown oily liquid consisting mostly of alkarsin (it is the substance of *arsenic* as containing the elements of *alcohol*, $C_4H_{12}As_2$ [5,11]) and other compounds. The top layer is a more watery liquid which is a solution of alkarsin in acetone, water and acetic acid [8]. Berzelius [12] changed 'alkarsin' used by Bunsen to 'cacodyl'. Kakodyl or cacodyl, was coined from the Greek roots for 'evil', 'pernicious', and 'odor'. In 1854, about one hundred years after 'Cadet's' was produced, it was published and clarified that the main component is tetramethyldiarsine ($Me_2As\text{-}AsMe_2$) [13]. The reaction mechanism has been extensively investigated [14], but it was not completely understood. However, generally, it is considered as follows: at first, potassium acetate is heated to yield acetone and potassium carbonate by their decomposition.

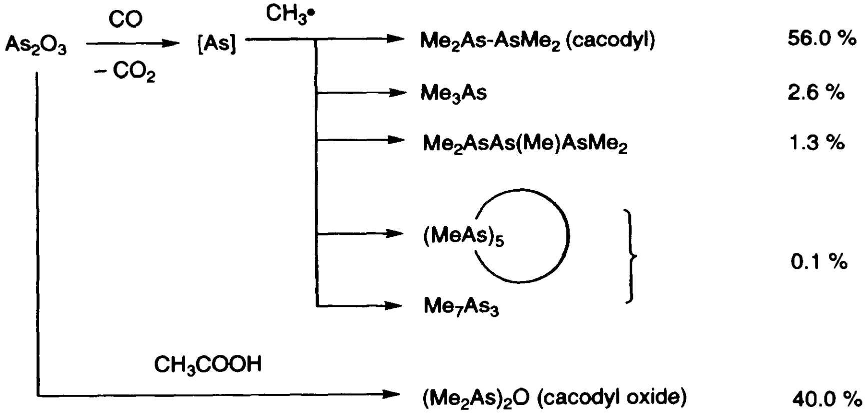
$$2CH_3COOK \xrightarrow{\text{heat}} (CH_3)_2C{=}O + K_2CO_3 \qquad (2\text{-}1)$$

$$(CH_3)C{=}O \xrightarrow{\text{heat}} 2CH_3\bullet + CO \qquad (2\text{-}2)$$

This reaction is well known in organic chemistry. The reaction requires a considerably high temperature, and the acetone probably may decompose to yield methyl radical and carbon monoxide [15]. The carbon monoxide reduces arsenic trioxide to yield arsenic. The arsenic reacts with the methyl radical to yield various kinds of organoarsenic compounds, and simultaneously hydrogen and various kinds of hydrocarbons were produced by thermal decomposition of acetone, as shown in Scheme 2.1 [17]. Hydrogen gives water by oxidation with arsenic trioxide. Potassium acetate, which does not react yet, gives acetic acid by hydrolysis with water. The acetic acid gives cacodyl oxide $(Me_2As)_2O$ by reaction with arsenic oxide [16]. The ratio of reaction products in one experiment is shown in Scheme 2.1 [17].

2.2 σ-BONDED ORGANOMETALLIC COMPOUNDS

Edward Flankland in Bunsen's laboratory synthesized organozinc compounds by direct reaction of alkyl iodide with zinc in 1849 [18,19]. This synthetic reaction



Scheme 2.1 [17]

method demonstrated two important results for the development of organometallic chemistry from that time on.

$$\mathrm{EtI} + \mathrm{Zn} \longrightarrow \mathrm{EtZnI} \qquad (2\text{-}3)$$

$$2\mathrm{EtZnI} \longrightarrow \mathrm{Et_2Zn} + \mathrm{ZnI_2} \qquad (2\text{-}4)$$

The first is to make possible the synthesis of various kinds of organometallic compounds by a transmetalation or a metathesis of organozinc compounds with other metals or metal compounds.

$$\mathrm{RM'} + \mathrm{M} \longrightarrow \mathrm{RM} + \mathrm{M'} \qquad (2\text{-}5)$$

$$\mathrm{RM'} + \mathrm{MX} \longrightarrow \mathrm{RM} + \mathrm{M'X} \qquad (2\text{-}6)$$

The second is the discovery of a direct reaction method of alkyl halides with metals. Various kinds of organometallic compounds with a metal except for zinc are also easily synthesized by this direct reaction method.

As the first transmetalation reaction, for example, organosodium compounds (1858) [20], organopotassium compounds (1858) [20], organorubidium compounds (1926) [21], organocesium compounds (1926) [21] and organothallium compounds (1870) [22], etc. are cited.

$$\mathrm{Et_2Zn} + 2\mathrm{M} \longrightarrow 2\mathrm{EtM} + \mathrm{Zn} \qquad (2.7)$$

$\mathrm{M} = \mathrm{K}, \mathrm{Na}, \mathrm{Rb}, \mathrm{Cs}$

$$3\mathrm{Et_2Zn} + 2\mathrm{Tl} \longrightarrow 2\mathrm{Et_3Tl} + 3\mathrm{Zn} \qquad (2.8)$$

As the metathesis, for example, organoantimony compound (1850) [23], organophosphorus compound (1857) [24], and organosilicon compound (1863) [25,26] are cited.

$$3\mathrm{Et_2Zn} + 2\mathrm{SbCl_3} \longrightarrow 2\mathrm{Et_3Sb} + 3\mathrm{ZnCl_2} \tag{2-9}$$

$$3\mathrm{Et_2Zn} + 2\mathrm{PCl_3} \longrightarrow 2\mathrm{Et_3P} + 3\mathrm{ZnCl_2} \tag{2-10}$$

$$2\mathrm{Et_2Zn} + \mathrm{SiCl_4} \longrightarrow \mathrm{Et_4Si} + 2\mathrm{ZnCl_2} \tag{2-11}$$

As the second direct reaction method, for example, organosodium compound (1858) [20], organocadmium compound (1861) [27,28], etc. are cited.

$$\mathrm{EtI} + 2\mathrm{Na} \longrightarrow \mathrm{EtNa} + \mathrm{Na} \tag{2-12}$$

$$2\mathrm{EtI} + 2\mathrm{Cd} \longrightarrow \mathrm{Et_2Cd} + \mathrm{CdI_2} \tag{2-13}$$

$$2\mathrm{EtI} + 2\mathrm{Mg} \longrightarrow \mathrm{Et_2Mg} + \mathrm{MgI_2} \tag{2-14}$$

$$3\mathrm{EtI} + 2\mathrm{Al} \longrightarrow \mathrm{Et_3Al} + \mathrm{AlI_3} \tag{2-15}$$

Organozinc compounds have been used as Flankland reagents until Grignard reagents began to be used early in the twentieth century. Grignard reagents have a reactivity that is higher than those for Flankland reagents, but their handling is easier and Grignard reagents have been gradually used in the place of the organozinc compounds as organosynthetic reagents.

Flankland synthesized organomercury compounds by the reaction of alkyl halides with sodium amalgam in 1852 [29].

$$2\mathrm{MeX} + 2\mathrm{Na/Hg} \longrightarrow \mathrm{Me_2Hg} + 2\mathrm{NaX} \tag{2-16}$$

Organomercury compounds are widely used for syntheses of organometallic compounds by the transmetalation or metathesis reaction similar to organozinc compounds. For example, organozinc compounds and organomagnesium compounds (1866) are prepared by the transmetalation of organomercury compounds with a metal [30,31].

$$\mathrm{Me_2Hg} + \mathrm{Zn} \longrightarrow \mathrm{Me_2Zn} + \mathrm{Hg} \tag{2-17}$$

$$\mathrm{Et_2Hg} + \mathrm{Mg} \longrightarrow \mathrm{Et_2Mg} + \mathrm{Hg} \tag{2-18}$$

However, as organomercury compounds have high toxicity, it was also gradually replaced by Grignard reagents.

Organosilicon compounds were prepared by the metathesis reaction of organozinc compounds with silicon tetrachoride as shown in eq. (2.11) in 1861. However, in 1941, Rochow [32–34] developed a direct reaction method with a copper catalyst, and a great amount of organosilicon compounds were easily prepared by this reaction method. Organosilicon compounds have become rapidly more numerous and 600 00 tons or more were produced in 1994. Thus they became the organometallic compound produced in the largest amount [34a,34b].

$$2MeCl \quad + \quad Si \quad \xrightarrow{Cu} \quad Me_2SiCl_2 \qquad (2\text{-}19)$$

Flankland [29] and Löwig [35] synthesized organotin compounds by the reaction of alkyl halides with tin and sodium amalgam in 1852. About 90 years later, in 1940, organotin compounds were used in large quantities, since it was found by Yngve [36] that they are useful as stabilizers for polyvinyl chloride resins. In 1993, these compounds were produced in amounts of 45 000 tons per year [36a].

In 1853, Löwig synthesized organolead compounds by the reaction of alkyl halides with lead and sodium amalgam similar to the organotin synthetic method [37]. In 1922, tetraethyllead was found to be useful for an antiknock agent by Midgeley and co-workers [38,39] at General Motor Company. Then, the production of organolead compounds became the largest in the organometallic compounds. But, in recent years, environmental problems have become severe, and in advanced countries, the uses of the compounds are restricted. At present, the production amounts drastically decreased [40–42a].

The synthetic method of producing tertiary alcohol by reaction of ketones with alkyl iodides in the presence of zinc is called the Saytzeff method. Barbier [43] attempted to synthesize dimethylheptenol from natural methylheptenone by this Saytzeff method in 1899.

$$Me_2C{=}CH(CH_2)_2C{=}O(Me) + MeI + Mg \longrightarrow Me_2C{=}CH(CH_2)_2C(Me)_2OMgI$$

$$\xrightarrow{H_2O} Me_2C{=}CH(CH_2)_2C(Me)_2OH \qquad (2.20$$

But, the intended compound is obtained by the reaction with magnesium in place of zinc because the reaction does not proceed with zinc. Afterwards, Barbier made Grignard, who was a student of his laboratory, try this research. Grignard, at first, thought to isolate the organomagnesium compound for the sake of the fundamental research. Grignard found the articles in which Flankland and Wanklyn had reported on how the organozinc compounds are easily handled in ether. Then he applied the ether to the stabilization of organomagnesium compounds and thus he was able to find compound known as the Grignard reagent. In 1900, he published his results [44–46]. Grignard reagents are able to be handled at ordinary temperatures and under atmospheric pressure, their reactivity is high and they are used in the widest range of reactions in organosynthetic chemistry. In 1912, he was awarded the Nobel

Prize for Chemistry for this discovery. The reaction of Barbier, as shown in eq. (2.20), is the reaction in which both halides and magnesium, which are the raw materials for Grignard reagents, directly react with the substrate. This reaction is called the Barbier reaction, to distinguish from the Grignard reaction [45,47].

Ziegler was interested in the reaction in which olefins insert into a metal–carbon bond, and then how triethylaluminum reacts with ethylene under high pressure. At one time, he did not get any polymers; only a dimer of butene was obtained. He investigated the cause in detail, and he found that it was due to the nickel compound adhered to the vessel because of insufficient cleaning of the vessel. Then, he investigated a wide range of metal compounds, and he found that ethylene is able to polymerize under ordinary temperatures and atmospheric pressure by adding titanium compounds as catalysts. These data were reported in *Angew. Chem.* in 1955 [48,49]. Natta was given these detailed reports and he succeeded in the polymerization of propylene. Afterward, he researched the area energetically and gave the concept of stereospecificity an assured status [50]. Research on Ziegler type catalysts has been carried out by very many researchers in the world. The production processes for polybutadiene and polyisoprene have been developed. Ziegler and Natta won the Nobel prize for development of the catalysts in 1963. From that time, organoaluminum compounds are used as various kinds of polymerization catalysts, and have been produced in similar amount to the organotin compounds.

2.3 METAL π-COMPLEXES

The first metal complex isolated as an organometallic compound was Zeise's salt, $K^+[C_2H_4PtCl_3]^-$. It was reported by Zeise in 1827 [5]. First, ethyl alcohol with a mixture of $PtCl_2$ and $PtCl_4$ was heated, then the excess alcohol is distilled off, and the aqueous KCl reacts with the residue to give the salt. Zeise reported that the salt is a compound of ethylene. But Liebig insisted on it being ethoxide because his elementary analysis data corresponded to that of a monohydrate, and he did not approve of the formation of ethylene complexes [51]. This salt forms usually a monohydrate and it is possible to remove the water of crystallization by treating in dry air or under vacuum [51]. In 1868, it became understood that this is the complex of ethylene by the fact that Birnbaum synthesized the Zeise salt by reaction of ethylene with H_2PtCl_6 [30,52]. Furthermore, the platinum salts containing propylene or amylene similar to the Zeise salt have also been synthesized. The π-coordination structure of the Zeise salt was presumed by the measurements of the IR spectrum and dipole moment [53]. In 1954, the structure was also determined by X-ray diffraction studies (Figure 2.1) [54,55].

In 1919, Hein [56] first synthesized a metal complex of an aromatic compound by reaction of PhMgBr with $CrCl_3$. However, this chromium complex was considered to be a complex having a σ-bond between chromium and benzene for a long time. This structure of the complex was not corrected until the structure of ferrocene, described subsequently, was established. In 1951, ferrocene (bis(π-cyclo-

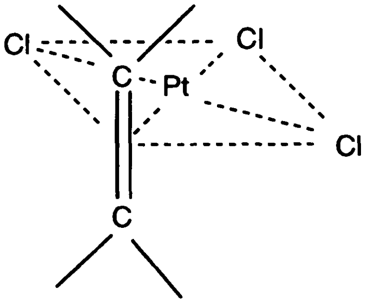


Figure 2.1. The structure of $[PtCl_3{\cdot}C_2H_4]^-$ [54,55]

pentadienyl)iron) was synthesized by two research groups. It may safely be said that the submission of their articles was almost at the same time. The paper of Kealy and Pauson [57] was received on August 7, 1951 and the paper of Miller *et al.* [58] was received on July 11 in the same year. Kealy and Pauson synthesized this complex by the reaction of a Grignard reagent with iron trichloride. The Grignard reagent has a reductive action to iron trichloride. For example, when phenylmagnesium bromide as a Grignard reagent reacts with iron trichloride, the iron trichloride is reduced quantitatively to iron metal and yields biphenyl. In the reaction of cyclopentadienylmagnesium bromide with iron trichloride, it is considered that the excess of cyclopentadienylmagnesium bromide reacts with iron dichloride that is obtained by the reduction of the iron trichloride with the Grignard reagent as shown in eq. (2.21,2.22) [57].

$$6PhMgBr + 2FeCl_3 \longrightarrow 3Ph\text{-}Ph + 2Fe + 3MgBr_2 + 3MgCl_2 \qquad (2.21)$$

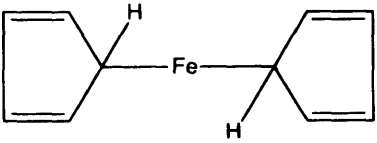
$$2C_5H_5MgBr + FeCl_2 \longrightarrow (C_5H_5)_2Fe + MgBr_2 + MgCl_2 \qquad (2.22)$$

On the other hand, Miller obtained ferrocene by the reaction of cyclopentadiene and iron powder under a nitrogen atmosphere at 300 °C.

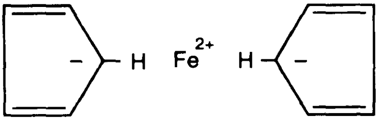
$$2C_5H_6 + Fe \xrightarrow{300\ ^\circ C} (C_5H_5)_2Fe + H_2 \qquad (2\text{-}23)$$

Both groups pointed out that the iron complex has abnormal stability (for example, it melts without decomposition at 172.5–173 °C) to heat and air as an organotransition metal complex. And both groups showed the σ-bonded complex between cyclopentadiene and iron as shown in compound **2-A**.

Kearly and Pauson [57] also considered an important contribution from a resonance form using an ionic bond **2-B** and intermediate forms.



2-A



2-B

Wilkinson *et al.* [59,60] proposed a sandwich structure because this compound is paramagnetic, the polarizability is 0, and the IR spectra showed only C—H stretching vibrations. Fisher and Phab [61] determined its structure by X-ray diffraction studies. Eiland and Pepinsky [62] and Dunitz and Orgael [63] also determined the sandwich structure by X-ray diffraction studies. Wilkinson and Fisher were awarded the Nobel prize for their achievements in this field in 1973 [64]. Wilkinson and Fisher made many contributions to chemistry over 20 years from the discovery of ferrocene to the winning of the Nobel Prize. For example, Wilkinson first found fluxional molecules of cyclopentadienyliron having a σ-bond in 1955 [65], and developed hydrogenation catalysts to be celebrated as the Wilkinson catalyst ($PhCl(PPh_3)_3$). This catalyst is a hydrogenation catalyst for olefins and acetylenes, and is used at ordinary temperatures and under atmospheric pressure. Fisher found a carbene complex ($(CO)_5W{=}C(OMe)Me$) [66] of a transition metal in 1964, and in 1973 also discovered a carbyne complex ($X(OC)_4W{\equiv}CRh$, $X =$ halogen).

Woodward *et al.* [67] named this bicylclopentadienyliron complex 'ferrocene' because this showed its similar reactivity to benzene, for example, Friedel–Crafts acylation easily proceeds as a substitution reaction. This name gave rise to metalocene as a general term for all sandwich complexes, and such metal compounds are called, for example, 'nickelocene' and 'cobaltocene'. These sandwich structures, like ferrocene, are synthesized not only for five-membered rings but also six-membered rings (chromium arene complexes), four-membered rings, seven-membered rings and 3–7 membered rings in which the two rings of the sandwich are different from each other. Metal complexes of bent-sandwich structures, bent at the metal as a center, and metal complexes of half-sandwich structures, having only

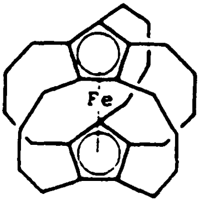


Figure 2.2 The structure of $[4_5](1,2,3,4,4)$ferrocenophane [69,69a]

one ring, were also synthesized. Furthermore, many metal complexes such as a multidecker sandwich structure in which rings are piled up threefold or more, a bent-polydecker sandwich structure which contains polymeric structures of bent-sandwich structure, are synthesized [68]. Compounds in which two rings of ferrocene are bonded with chains such as alkyl groups are called ferrocenophanes. Various kinds of ferrocenophane have been synthesized. In 1986, Hisatome and coworkers [69] synthesized $[4_5](1,2,3,4,5)$ferrocenophane (superferrocenophane, perferrocenophane, superbridged ferrocenophane) which is a pentabridged ferrocenophane and the structure was determined by X-ray diffraction studies (Figure 2.2).

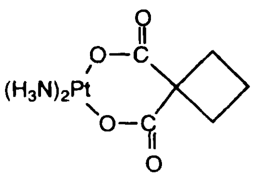
2.4 ORGANOMETALLIC COMPOUNDS HAVING PHYSIOLOGICAL ACTIVITIES

Many organometallic compounds having physiological activities have been found. In these compounds, the compounds which are utilized for their strong toxicities were poison gases, such as cacodyl described above, which is an organoarsenic compound having highly toxic properties [6,7,30]. In 1914, the poison gas used in World War I was lewisite ($ClCH{=}CHAsCl_2$) which is also an organoarsenic compound. The research on organoarsenic, organozinc and organomercury compounds took a heavy toll of human lives. It is said that Bunsen and Flankland were also sacrifices in the research of these compounds. In 1995, sarin ($MeP({=}O)(F)O\text{-}t\text{-}Bu$) and VX ($MeP({=}O)(OEt)SCH_2CH_2N(t\text{-}Bu)_2$) were the nerve gases used in a poison gas plot in Japan. These poison gases are organophosphorus compounds and their toxicities are 20 times (sarin) and 40 times (VX) higher than that of hydrocyanic acid gas [60b]. Organomercury compounds are known, especially, for their high toxicities, and it is believed they become nonpoisonous if they are converted to the inorganic mercury compounds by treating them. Moreover, as a common sense on the organometalllic compounds, generally, these compounds are largely liable. It was considered that they will become inorganic compounds by gradually decomposing in air. But environmental pollution by organomercury compounds caused harm to the public in Japan in the 1950s and in Sweden in the 1960s [70–73]. This is because even if the organomercury compounds were converted to inorganic mercury compounds by decomposition, a highly toxic methyl mercury is produced from the inorganic mercury compounds by the action of microorganisms in the mud at the bottom of the sea or lake, and organisms intake methylmercury. This reaction is named 'biological methylation' by Challenger [72,74] in 1945. This reaction is a methylation by the action of organisms on the compounds of arsenic, selenium, tellurium, cobalt and mercury. The cause of this environmental pollution became gradually apparent with the clarification of biological methylation [73].

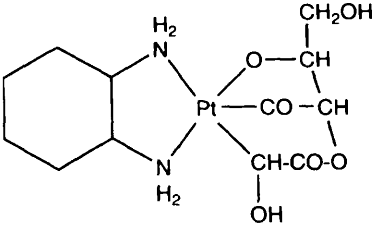
Organomercury compounds, organoarsenic compounds and organotin compounds show high toxicities to organisms. However, if these show high toxicity only to specific organisms, these can be used as germicides, herbicides, insecticides, pharmaceuticals and agricultural chemicals. In 1908, Ehrlich developed salvarsan $(4\text{-}HO(3\text{-}NH_2)C_6H_3{-}As{-})_6$. This is well-known as a specific remedy for syphilis, and it had been widely used, also, as a medicine for sleeping sickness in Africa. However, recently it has been replaced by antibiotics such as penicillin [30,75].

In 1948, vitamin B_{12} was isolated from the liver as red crystals. In 1961, it was determined that it forms a chelate structure having a $Co{-}CH_2$ bond by X-ray diffraction studies. Then vitamin B_{12} becomes the first compound having a metal–carbon bond to be discovered in natural compounds [75a]. The total synthesis of vitamin B_{12} was achieved in 1972 by the result of one joint research work with one hundred researchers from nineteen countries at Harvard University and Zürich University over a period of eleven years [75b].

In 1968, Rosenberg and co-workers [76,77] passed low alternating current voltage using platinum electrodes through a culture medium containing *E coli* in order to investigate the effect of electric current on cell division. *E coli* cell division stopped. However, growth was not checked and they grew up to form fibrous cells attaining a length of 300 times that of an ordinary cell. They investigated the cause of the cell division in detail, and they found that the electric field does not act directly on the bacilli. Instead the electrolysis products of the platinum used as an electrode was active. They investigated the various kinds of compounds that act only to produce fibrous cells and to stop cell divisions. In 1919, they found that cisplatin ($\mathit{cis}(Pt(NH_3)_2Cl_2)$) is a clinically important anticancer drug, being especially effective for the management of testicular, ovarian, and head and neck



2-C



2-D

cancers [76,77]. It is one of the most widely used antitumor drugs at the present time. However, cisplatin has side effects such as nephrotoxicity, gastrointestinal toxicity, nausea, emesis and bradyacusia. Many platinum complexes have been synthesized for the sake of decreasing these side effects. In these complexes, carboplatin (**2-C**) has similar anticancer activity to cisplatin and the side effects are much lower, and it is called an anticancer drug of the secondary generation.The platinum complex (**2-D**) of cisdiamine with vitamin C is an organometallic compound which shows similar anticancer activities [77a–e].

2.5 METALCARBONYL COMPOUNDS

The Solvay process, which is a manufacturing process for sodium carbonate, was discovered in 1861. The operation of a production plant started at Couillet in Belgium in 1865. The reaction is, on the whole, to obtain sodium carbonate by reaction of calcium carbonate with sodium chloride as shown in eq. (2.24).

$$CaCO_3 \quad + \quad 2NaCl \longrightarrow Na_2CO_3 \quad + \quad CaCl_2 \qquad (2\text{-}24)$$

In the operation, it was found that nickel, which was used in a valve, was abnormally corroded. Mond [78] investigated the corrosion of the valves in the Solvay process in detail. Consequently, he found that carbon monoxide, which was contained in carbon dioxide from the interim raw materials, reacts with the nickel. Thus he found the first metal carbonyl, with two components of metal and carbonyl, in 1890. For a metal carbonyl with three components, in 1869, Schlutzerberger [79] found $Pt(CO)Cl_2$ prior to the discovery of $Ni(CO)_4$.

$$Ni \quad + \quad 4CO \longrightarrow Ni(CO)_4 \qquad (2\text{-}25)$$

As the reverse reaction proceeds when nickel carbonyl is heated at a temperature of 150 °C or more, the formation and decomposition reactions of nickel carbonyl began to be utilized in the manufacture of highly pure nickel [79a]. Following the discovery of nickel carbonyl, iron carbonyl ($Fe(CO)_5$) [84] was found in 1891, and various other kinds of metal carbonyls have now been found [80a].

In around 1925, the Fisher–Tropsh process, which synthesizes mainly liquid hydrocarbons by the reaction of carbon monoxide with hydrogen at 180–300 °C and under 1–300 atm in the presence of nickel, cobalt and iron compounds as catalysts, was developed [81,81a,81b]. This process was used as the process for synthetic petroleum in Germany. However, at present, the production has been continued only in South Africa as state policy. This reaction is revealed to have the action of metal carbonyls as intermediates of the catalysts. In 1938, Roclen [82] developed the oxo process which produced aldehydes by the reaction of olefins with carbon monoxide and hydrogen in the presence of cobaltcarbonyl type catalysts.

Reppe [83] developed the 'Reppe reaction' of carbonylation, vinylation, ethynylation and cyclization by reaction of acetylene with carbon monoxide, water, alcohols, amines, aldehydes and ketones, etc. In 1952, the reaction of olefins in place of acetylene, in the presence of metal carbonyl catalysts, produces alcohols. This process is called the new Reppe process, and butanol has been industrially produced by this process since around 1960.

$$CH_2{=}CH{-}CH_3 + 3CO + 2H_2O \longrightarrow C_4H_9OH + 2CO_2 \qquad (2\text{-}26)$$

Roth and co-workers [84] at the Monsanto company developed an acetic acid production process by the reaction of methyl alcohol with carbon monoxide in the presence of rhodium carbonyl as the major catalyst.

$$CH_3OH + CO \xrightarrow[\text{Rh cat.}]{175\ ^\circ\text{C, initial 50 psi}} CH_3COOH \qquad (2\text{-}27)$$

2.6 OTHERS

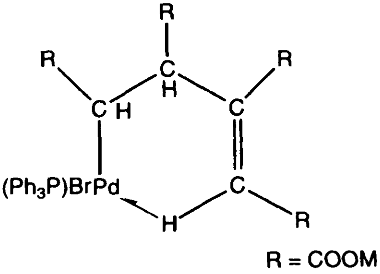
In 1956, H. C. Brown [85] found hydroboration which produces organoboron compounds by the addition of boron hydrides such as diborane and alkyl borane to an olefin. This hydroboration is very reactive, and it easily gave organometallic compounds.

$$B_2H_6 + 2RCH{=}CH_2 \longrightarrow 2RCH_2{-}CH_2BH_2 \qquad (2\text{-}28)$$

Similarly, the reactions of olefins with metal hydrides, such as silicon hydrides, germanium hydrides, tin hydrides and lead hydrides, were also found. These reactions are called hydrosilylation, hydrogermanation, hydrostannation and hydroplumbylation, respectively. These reactions easily proceed even if the R in eq. (2.28) are functional groups. Then these reactions are conveniently used for syntheses of organometallic compounds having a functional group by a one-stage reaction.

In 1965, Allen and Senoff [86] first found a nitrogen complex ($[Ru(NH_3)_5N_2]^{2+}$ and shortly after, many nitrogen complexes were successively synthesized.

In 1983, Brookhart and Green [87] found a new bond called 'agostic' in which hydrogen bonds with carbon and a transition metal simultaneously. Since this bond is a two-electron three-center bond, it is an electron-deficient bond. Both C—H and M—H bonds are longer by 5–20 % than ordinary bonds and the reactivity is high



2-E

[88]. It is considered that Ti in Ziegler–Natta catalysts forms an agostic bond in the olefin polymerization. The 'agostic' bond is, for example, the bond of the compound shown in **2-E** [89].

In September 1985, Smalley and Kroto *et al.* found that when a carbon cluster is irradiated, the C_{60} peak is abnormally large in the mass spectrum, and they presumed the formation of the compounds of a soccer ball structure. They named it Buckminsterfullerene from Buckminster Fuller, the designer of the circular dome. It has now been abbreviated to buckyball or fullerene. C_{60} is a semiconductor, a high electrical conductor like metals by adding elements such as an alkali metal, and a superconductor and highly ferromagnetic by mixing organoamine compounds. It is investigated for various kinds of uses such as new functional polymers by bonding with polymers, new catalysts, photoconductive materials, pharmaceuticals, and diagnostic medicines.

Fullerenes are not only C_{60} but also C_{70}, C_{78}, C_{82}, C_{84} and cylindrical carbon nanotubes, etc. C_{60} is gradually being produced in large quantities, the price is becoming significantly lower, the number of researchers is increasing, and various kinds of properties have been revealed [89c,89d].

C_{60} has a large electron affinity (2.8 eV), a low ionization potential (7.6 eV) and is a highly reactive molecule. In particular, [1 + 2]-, [2 + 2]-, [3 + 2]- and [4 + 2]-cyclic additions to the double bond of C_{60} easily proceed, and in addition, ionic additions, radical addition, halogenations, hydrogenations and formation reactions of transition metal complexes also proceed easily [89e]. As described in a later chapter on organotransition metal compounds, C_{60} easily forms π-complexes of a transition metal with its carbon–carbon unsaturated bond.

The large-scale petrochemicals industry developed in the 1950s–1970s, but current chemical industries tend to focus their attention on fine chemicals. In organometallic chemistry an emphasis on the development of new materials such as functional polymers, electronic materials, pharmaceuticals and cosmetics, and organic synthetic methods with organometallic compounds are noted [90,91].

Finally, Table 2.1 shows major events in the history of organometallic chemistry in chronological order.

Table 2.1 Historical development in organometallic chemistry [1,2,30,92,93]

1760	The first preparation of organometallic compounds, 'Cadet's fuming arsenical liquid' [7].
1827	Zeise's salt discovered, $K^+(C_2H_4PtCl_3)^- \cdot H_2O$.
	The first transition metal organometallic compound [5].
1837	The study of the detailed nature and reactions of cacodyl and its derivatives (Bunsen) [6].
1849	The preparation of the first organozinc compounds, EtZnI and Et_2Zn (Flankland) [18].
1852	The preparation of the first organomercury compounds, Me_2Hg (Flankland) [29].
1853	The preparation of the first organolead compounds, Et_4Pb, Et_3PbI (Löwig) [37].
1854	The determination of the true structure of cacodyl [13].
1859	The preparation of the first organoaluminum compounds, Et_2AlI, $EtAlI_2$ [94].
1863	The preparation of the first organosilicon compound, Et_4Si, [25,26].
1868	Schutzenberger prepared the first carbonyl complex, $[Pt(CO)_2Cl]_2$ [78].
1890	The preparation of $Ni(CO)_4$ [79].
1891	The preparation of $Fe(CO)_5$ [80].
1900	The preparation and use of Grignard reagents [44].
1908	Ehrlich developed salvarsan $(4\text{-}HO(3\text{-}NH_2)C_6H_3{-}\overset{\mid}{As}{-})_6$ [74a].
1909	The preparation of the first organotransition metal compound having a σ-bond, Me_3PtI [95].
1917	The synthesis of organolithium compounds; Development of closed-tube synthetic methods [96].
1919	The synthesis of diphenylchromium compound (Hein complex) [56].
1922	The discovery of the antiknock properties of tetraethyllead [39].
1925	The Fischer–Tropsch process is developed [81].
1930	Reihlen prepared 1,3-butadieneirontricarbonyl [97].
1931	The preparation of the first organotransition metal hydride, $Fe(CO)_4H_2$ [98].
1938	Roelen discovers the cobalt-catalyzed oxo-process [82].
	W. Reppe starts working on the transition metal catalyzed reaction of acetylene. Reppe reactions [83].
	Lucas and Winstein studied silver–olefin complexes [99].
1941	The discovery of the direct synthetic method for organosilicon compounds, (Rochow) [100].
1948	Reppe describes the catalytic cyclotrimerization of acetylene to cyclooctatetraene [101].
1951	The discovery of ferrocene [57,58].
1952	The sandwich structure and aromatic nature of ferrocene [59,60].
1953	The proposal of molecular orbital theory to explain the bonding in electron-deficient compounds [102].
1955	The discovery of the Ziegler process [48].
	Cotton and Wilkinson discover fluxional behavior [65].
1956	The discovery of the hydroboration reaction [85].
1959	The synthesis of optically active organosilicon compounds [103].
1961	Crowfoot-Hodgkin elucidates the structure of the coenzyme vitamin B_{12} [75a].
1962	Vaska discovers the 'Vaska complex' $(PPh_3)_2Ir(CO)Cl$ [104].
1964	Fischer isolated the first carbene complex $(CO)_5W{=}C(OMe)Me$ [66].
	Discovery of olefin metathesis reaction (Banks) [105].

(continued)

Table 2.1 *(continued)*

1965	Wilkinson and Coffey independently discover 'the Wilkinson hydrogenation complex' $(PPh_3)_3RhCl$ [106]. Allen and Senoff discover the first dinitrogen complex [86].
1971	Monsanto develops rhodium-catalyzed acetic acid process [84].
1972	The total synthesis of vitamin B_{12} [75b].
1973	Fischer prepares the first carbyne complex $(CO)_5W{\equiv}C(OMe)Me$ [107].
1975	DuPont's adipontrile synthesis by catalytic addition of HCN to butadiene [108].
1983	The concept of 'agostic' structure is formulated by Brookhart and Green [87].
1985	The discovery of fullerene [89a,89b].

REFERENCES

[1] E.G. Rochow, D.T. Hurd and R.N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley, New York, 1957.
[2] J.J. Eisch, *The Chemistry of Organometallic Compounds, The Main Group Elements*, Macmillan, New York, 1967.
[3] A. Yamamoto, *Organometallic Chemistry, Fundamental Concepts and Applications*, Shokabo, Tokyo, 1982.
[4] A. Yamamoto, *Organotransition Metal Chemistry, Fundamental Concepts and Applications*, John Wiley, New York, 1986.
[5] W.C. Zeise, *Pogg. Ann.*, **9** (1827) 632; **21** (1831) 497.
[6] R. Bunsen, *Liebigs Ann. Chem.*, **24** (1837) 471.
[7] L.C. Cadet de Gassicourt, *Mem. Mat. Phys.*, **3** (1760) 363, 623.
[8] J.S. Thayer, *J. Chem, Educ.*, **43** (1966) 594.
[9] R. West, Extra-Curriculum Lecture in Osaka University in Japan, 1966.
[10] L.J. Thenard, *Liebigs Ann. Chem.*, **52** (1804) 54.
[11] R. Busen, *Liebigs Ann. Chem.*, **31** (1839) 175.
[12] J.J. Berzelius, *Jahresbericht*, **20** (1841) 526.
[13] A. Cahours and A. Riche, *Liebigs Ann. Chem.*, **92** (1854) 301.
[14] A. Valeur and P. Gaillot, *Compt. Rend.*, **185** (1927) 956.
[15] M. Dehara, *Yuki Gosei Kagaku Kyokaishi*, **20** (1962) 730.
N.T.M. Wilsmore, *J. Chem. Soc.*, (1907) 1938.
[16] R.C. Fuson and W. Shive, *J. Am. Chem. Soc*, **69** (1947) 559.
[17] E.G. Rochow, D.T. Hurd and R.N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley, New York, p. 208 1957.
[18] E. Frankland, *Liebigs Ann. Chem.*, **71** (1849) 171.
[19] J.S. Thayer, *J. Chem. Educ.*, **46** (1969) 764.
[20] J.A. Wanklyn, *Liebigs Ann. Chem.*, **108** (1858) 67.
[21] A. von Grosse, *Chem. Ber.*, **59** (1926) 2646.
[22] C. Hansen, *Chem. Ber.*, **3** (1870) 9.
[23] C. Löwig and E. Schweizer, *Liebigs Ann. Chem.*, **75** (1850) 315.
[24] A. Cahours and A.W. Hofmann, *Liebigs Ann. Chem.*, **104** (1857) 29.
[25] C. Friedel and J.M. Crafts, *Liebigs Ann. Chem.*, **127** (1863) 28.
[26] C. Friedal and J.M. Crafts, *Liebigs Ann. Chem.*, **136** (1865) 203.
[27] G. Buckton and W. Odling, *Proc. Roy. Soc.*, **14** (1865) 19.
[28] E. Frankland, *J. Chem. Soc.*, **13** (1861) 177.
[29] E. Frankland, *Phil. Trans.*, **142** (1852) 417.
[30] J.S. Thayer, *Adv. Organomet. Chem.*, **13** (1975) 1.

[31] J.A. Wanklyn, *Liebigs Ann. Chem.*, **140** (1866) 353.
[32] E.G. Rochow, *J. Chem. Educ.*, **43** (1966) 58.
[33] R. Müller and E.G. Rochow, *J. Chem. Educ.*, **42** (1965) 41.
[34] M.P. Clarke, *J. Organomet. Chem.*, **376** (1989) 165.
[34a] *SRI Chemical Economics Handbook Marketing Research Report, Silicones*, 583.0100A, Jan. 1993.
[34b] *Silicon and Their Uses*, Toshiba Sillicones Co.Ltd., 1994.
[35] C. Löwig, *Liebigs Ann. Chem.*, **84** (1852) 308.
[36] V. Yngve, *U.S. Patent*, 2,219,463 (1940) .
[36a] *SRI Chemical Economics Handbook Marketing Research Report, Organometallics*, 681.7000A, Feb. 1995.
[37] C. Löwig, *Liebigs Ann. Chem.*, **88** (1853) 318.
[38] A.B. Garrett, *J. Chem. Educ.*, **39** (1962) 414.
[39] T. Midgeley and T.A. Boyd, *Ind. Eng. Chem.*, **58** (1922) 894.
[40] Y. Segawa, *Petrotech*, **11** (1988) 1105.
[41] K. Tachiki, *Petrotech*, **11** (1988) 804.
[42] M. Matsubara, *Petrotech*, **11** (1988) 1040.
[42a] *SRI Chemical Economics Handbook Marketing Research Report, Gasoline Octane Improvers*, 543.7500A, May 1994.
[43] P.A. Barbier, *C.R. Acad. Sci*, **128** (1899) 110.
[44] V. Grignard, *C.R. Acad. Sci*, **130** (1900) 1322.
[45] P.R. Jones and E. Southwick, *J. Chem. Educ.*, **47** (1970) 290.
[46] M. Kumada, *Kagaku*, **44** (1989) 34.
[47] C. Blomberg and F.A. Hartog, *Synthesis*, (1977) 18.
[48] K. Ziegler, E. Holtzkampf, H. Breil and H. Martin, *Angew. Chem.*, **67** (1955) 426, 541.
[49] A. Yamamoto, *Kagaku*, **44** (1989) 14.
[50] G. Natta, *Angew. Chem.*, **76** (1964) 553.
[51] J.S. Thayer, *Chem. Educ.*, **46** (1969) 442.
[52] K. Birnbaum, *Liebigs Ann. Chem.*, **145** (1868) 68.
[53] L. Chatt and L.A. Duncanson, *J. Chem. Soc.*, (1953) 2939.
[54] J.A. Wunderlich and D.P. Mellor, *Acta Cryst.*, **7** (1954) 131; **8** (1955) 57.
[55] G.B. Bokij and G.A. Kukita, *Acta Cryst.*, **10** (1957) 786.
[56] F. Hein, *Chem. Ber.*, **52** (1919) 195.
[57] T.J. Kealy and P.L. Pauson, *Nature*, **168** (1951) 1039.
[58] S.A. Miller, J.A. Tebboth and J.F. Tremaine, *J. Chem. Soc.*, (1952) 632.
[59] G. Wilkinson, M. Rosenblum, M.C. Whiting and R.B. Woodward, *J. Am. Chem. Soc.*, **74** (1952) 2125.
[60] G.B. Kauffman, *J. Chem. Educ.*, **60** (1983) 185.
[61] E.O. Fischer and W. Pfab, *Z. Naturforsch.*, **B7** (1952) 4971.
[62] P.F. Eiland and R. Pepinsky, *J. Am. Chem. Soc.*, **74** (1952) 378.
[63] J.D. Dunitz and L.E. Orgel, *Nature*, **171** (1953) 121.
[64] D. Seyferth and A. Davison, *Science*, **182** (1973) 699.
[65] G. Wilkinson and T.S. Piper, *J. Inorg. Nucl. Chem.*, **2** (1956) 23.
F.A. Cotton, *J. Organomet Chem.*, **100** (1975) 29.
[66] E.O. Fischer and A. Maasbol, *Angew. Chem. Int. Ed. Engl.*, **3** (1964) 580.
[67] R.B. Woodward, M. Rosenblum and M.C. Whiting, *J. Am. Chem. Soc.*, **74** (1952) 3458.
[68] P. Jutzi, *Pure Appl. Chem.*, **61** (1989) 1731.
[69] M. Hisatome, J. Watanabe, K. Yamakawa and Y. Iitaka, *J. Am. Chem. Soc.*, **108** (1986) 1333.
[69a] M. Hisatome, J. Watanabe, Y. Kawajiri and K. Yamakawa, *Organometallics*, **9** (1990) 497.

[69b] A.T. Tu, *Kagaku*, **49** (1994) 710.
[70] J.M. Wood, F.S. Kennedy and C.G. Rosen, *Nature*, **220** (1968) 173.
[71] S. Jensen and A. Jernelöv, *Nature*, **223** (1965) 753.
[72] J.S. Thayer, *J. Chem. Educ.*, **50** (1973) 390.
[73] D.H. Klein, *J. Chem. Educ.*, **49** (1972) 7.
[74] F. Challenger, *Chem. Rev.*, **36** (1945) 315.
F. Challenger, *Quart. Rev.*, **9** (1955) 255.
[74a] P. Ehrlich and A. Bertheim, *Chem. Ber.*, **45** (1912) 756.
[75] J.S. Thayer, *J. Chem. Educ.*, **48** (1971) 806.
[75a] P.G. Lenhart and D. Crowfoot-Hodgkin, *Nature*, **192** (1961) 937.
[75b] T. Ando (Translator), *Serendipity*, Kagaku Dojin, Kyoto, 1993.
[76] B. Rosenberg, L. von Camp and T. Kriegas, *Nature*, **203** (1965) 698.
[77] B. Rosenberg, J.E. Trosko and V.H. Mansour, *Nature*, **222** (1969) 385.
[77a] H. Yamazaki and Y. Wakatsuki, *Yuki Kinzoku no Kagaku*, Japanese Chem. Soc., ed., Dai Nippon Tosho, Tokyo, 1989.
[77b] A. Pasini and F. Zunino, *Angew. Chem. Int. Ed. Engl.*, **26** (1987) 615.
[77c] S.E. Sherman, D. Gibson, A.H.-J. Wang and S.J. Lippard, *Science*, **230** (1985) 412.
[77d] P. Köpf-Maier, *Naturw.*, **74** (1987) 374.
[77e] T. Shimura and H. Okuno, *Kagaku*, **46** (1991) 685.
[78] L. Mond, C. Langer and F. Quincke, *J. Chem. Soc.*, **57** (1890) 749.
[79] M.P. Schutzenberger, *Liebigs Ann. Chem.*, **15** (1868) 100.
[79a] R.D. Rausch, *J. Organomet. Chem.*, **383** (1990) 1.
[80] L. Mond and C. Langler, *J. Chem. Soc.*, **59** (1891) 1090.
[80a] H.E. Podall, *J. Chem. Educ.*, **38** (1961) 187.
[81] F. Fisher and H. Tropsch, *German Patent*, 411,416 (1922) , 484,337 (1925).
[81a] C.K. Rofer-DePoorter, *Chem. Rev.*, **81** (1981) 447.
[81b] W.A. Herrmann, *Angew. Chem. Int. Ed.*, **21** (1982) 117.
[82] O. Roelen, *German Patent* 849,548 (1938), *Angew. Chem.*, **60** (1948) 62.
[83] W. Reppe, *Neue Entwicklungen auf dem Gebiete der Chemie des Acetylens und des Kohlenoxyds*, Springer Verlag, New York, 1949.
[84] J.F. Roth, J.H. Craddock, A. Hershman and F.E. Paulik, *Chem. Tech.*, **1** (1971) 600.
[85] H.C. Brown and B.C.S. Rao, *J. Am. Chem. Soc.*, **78** (1956) 569.
[86] A.D. Allen and C.V. Senoff, *Chem. Commun.*, (1965)621.
[87] M. Brookhart and M.L.H. Green, *J. Organomet. Chem.*, **250** (1983) 395.
[88] I. Omae, *J. Organomet. Lib.*, ***18***, *Organometallic Intramolecular-coordination Compounds*, Elsevier, Amsterdam, 1986.
[89] D.M. Roe, P.M. Bailey, K. Moseley and P.M. Maitilis, *J. Chem. Soc. Chem. Commun.*, (1972)1273.
[89a] R.E. Smalley and E. Ohsawa, *Gendai Kagaku*, April (1992) 28.
[89b] H. Shinohara, *Kagaku*, **47** (1992) 620.
[89c] *Nikkei Sangyo Shinbun*, August 9, 1995.
[89d] S. Yamago and E. Nakamura, *Kobunshi*, **44** (1995) 451.
[89e] M. Iyoda and M. Yoshida, *Yuki Gosei Kagaku Kyokaishi*, **53** (1995) 756.
[90] G.W. Parshall, *Organometallics*, **6** (1987) 687.
[91] G.W. Parshall, W.A. Nugent, D.M.-T. Chan and W. Tam, *Pure Appl. Chem.*, **57** (1985) 1809.
[92] K.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, California, 1987.
[93] Ch. Elschenbroich and A. Salzer, *Organometallics*, VCH, Weinheim, 1989.
[94] W. Hallwachs and A. Schafarik, *Liebigs Ann. Chem.*, **109** (1859) 207.
[95] W.J. Pope and S.J. Peachey, *J. Chem. Soc.*, **95** (1909) 571.
[96] W. Schlenk and J. Holtz, *Chem. Ber*, **50** (1917) 262.

[97] H. Reihlen, A. Gruhl, G. von Hessling and O. Pfrengle, *Liebigs Ann. Chem.*, **482** (1930) 161.
[98] W. Hierber and F. Leutert, *Naturw.*, **19** (1931) 360.
[99] S. Winstein and H.J. Lucas, *J. Am. Chem. Soc.*, **60** (1938) 836.
[100] E.G. Rochow, *J. Am. Chem. Soc.*, **67** (1945) 963; *U.S. Patent* 2,380,996 (1945).
H. Sano, *Kagaku Keizai*, May (1990) 63.
[101] W. Reppe, O. Schlichtung, K. Klager and T. Toepel, *Liebigs Ann. Chem.*, **560** (1948) 104.
[102] P.H. Lewis and R.E. Rundle, *J. Chem. Phys.*, **21** (1953) 986.
[103] L.H. Sommer and C.L. Frye, *J. Am. Chem. Soc.*, **81** (1959) 1015.
[104] L. Vaska and J.W. Diluzio, *J. Am. Chem. Soc.*, **84** (1962) 679.
[105] R.L. Banks and G.C. Bailey, *Ind. Eng. Chem. Prod. Res. Develop.*, **3** (1964) 170.
[106] J.F. Young, J.A. Osborn, F.H. Jardine and G. Wilkinson, *Chem. Commun.*, (1965) 131.
R.S. Coffey, *British Patent*, 1,121,642 (1965)
[106a] T. Ando (Translator), *Serendipity*, Kagaku Dojin, 1993.
[107] E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner and H. Lorenz, *Angew. Chem. Int. Ed. Engl.*, **12** (1973) 564.
[108] C.A. Tolman, R.J. McKinney, W.C. Seidel, J.D. Druliner and W.R. Stevens, *Adv. Catal.*, **33** (1985) 1.

3 Organolithium Compounds

3.1 INTRODUCTION

Organolithium compounds are widely used along with Grignard reagents as organosynthetic reagents. These reagents are generally utilized on the account of their high reactivities. The most representative reactions of Grignard reagents are to synthesize the secondary or tertiary alcohols by the addition reaction to the carbonyl groups of aldehydes, ketones and esters. Many organometallic compounds described in later chapters are also used as organosynthetic reagents; organosilicon compounds are used for selectively bonding with a variety of organic compound unsaturated groups such as allyl, vinyl, alkynyl and allene, organoaluminum compounds are used for mild reduction, organotitanium compounds are used for elimination of oxygen atom, methylenation and *gem*-dimethylation of carbonyl groups, organocopper compounds are used for addition to α,β-unsaturated carbonyl compounds and selective substitution reaction with halogen of the carbonyl compounds having a halogen atom, and organoboron compounds are used for an asymmetric reduction. These reactions are also widely used as the most representative reactions.

The reactions with organolithium compounds proceed similarly to Grignard reactions; however, they are used especially for reactions in which the reactivities of the Grignard reaction are low. Organolithium compounds are applied as the organosynthetic reagents for pharmaceuticals, agrochemicals and perfumes. Organolithium compounds are also largely used as polymerization catalysts for synthetic rubbers [1–4].

3.2 LITHIUM

The lithium content of the Earth's crust is estimated to be 20 ppm [5]. Ocean water contains about 0.17 ppm, whereas many natural brines have several hundred ppm [3]. The representative lithium ores are spondumene ($Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$, with a theoretical LiO_2 content of 8.03 %, commercial ores usually contain 4–7 %), pentalite ($Li_2O{\cdot}Al_2O_3{\cdot}8SiO_2$, with a theoretical LiO_2 content of 4.88 %, commercial ores usually contain 3.4–4.5 %) and lepidolite ($2(K{\cdot}Li)F{\cdot}Al_2O_3{\cdot}3SiO_2$, with a LiO_2 content of 3–4 %). Spondume is the most important lithium mineral ore and is characterized by a high lithium content, extensive deposits, and processing advantages [1,2].

Spondumene is the principal source of lithium for its production. On heating to about 1075–1100 °C, an α-isomer of the spondumene converts to the much more reactive β-isomer. It is added to 93 % sulfuric acid and the mixture is roasted to about 250 °C to form soluble lithium sulfate. The excess sulfuric acid is neutralized with ground limestone and is then filtered and lithium carbonate is precipitated at 90–100 °C with a 28 wt% soda ash solution. Hydrochloric acid is added to the lithium carbonate to give lithium chloride, and the anhydrous lithium chloride is produced by heating at 250–300 °C. Industrial electrolysis is carried out using a LiCl (52 mol%)–KCl (48 mol%) electrolyte mixture at 400–420 °C with 850–900 A and at 8–9 V in the cell. Lithium is deposited on the steel cathode under an argon atmosphere. The current efficiency is 85–90 % [1,2,6,7].

Shikoku Kogyo Shikensho developed a microporous manganese oxide type adsorbant which is able to separate lithium from sea water at a cost of about the market price in 1994 [8].

The properties of lithium are shown in Table 3.1 [1–3]. Lithium has an atomic weight of 6.941 and is the lightest element in the metals. In the alkali metal group, lithium has the highest mp (180.54 °C), bp (1342 °C) and heat capacity, the smallest ionic radius (60 pm), and is the hardest. Its ductility is about the same as that of lead [1,2]. Lithium reacts with water with formation of hydrogen which ignites under normal conditions only if the metal is finely divided. The reaction of hydrogen and lithium readily gives a hydride, LiH, and lithium reacts with nitrogen, even at ordinary temperatures, to form nitride, Li_3N. Lithium burns when heated in oxygen to form the oxide, Li_2O. Lithium remains untarnished in dry air but in moist air its surface becomes coated with a mixture of LiOH, $LiOH{\cdot}H_2O$, Li_2CO_3 and Li_3N. Lithium is less active than the other alkali metals. But lithium metal can react with silicates (e.g. sand and concrete) and carbon dioxide. Therefore, sand and carbon

Table 3.1 Physical properties of lithium [1–3]

Property	Value
melting point, °C	180.54
boiling point, °C	1342
crystal structure	body center cubic
density, 20 °C, g/cm^3	0.534
hardness, Mohs	0.6
heat of fusion, J/g	431.4
heat of vaporization, kJ/g	22.705
specific heat (20 °C to 190 °C), J/g	3.3–4.2
electron affinity, kJ/mol	52.3
electrical resistivity at 20 °C, mW cm	9.446
ionization energy, kJ/mol (eV)	5.19 (5.37)
atomic radius (in the metal), pm	122.5
ionic radius, pm	60

dioxide fire extinguishers are ineffective as fire-fighting agents for lithium fires. Powdered limestone (calcium carbonate) and fire-extinguishing powders based on lithium chloride are suitable for fighting lithium fires [3].

Lithium metal dissolves readily in liquid ammonia, the concentration of the saturated solution at −33.2 °C being 9.8 wt %. The solution of lithium in ammonia is used for Birch reduction in organic synthesis. The largest application of lithium metal is in the production of organolithium compounds, principally butyllithium and lithium hydride. Butyllithium is useful as homogenous catalysts in the stereospecific polymerization of conjugated polyenes such as 1,3-butadiene, isoprene and styrene. Lithium is used as a reducing agent in organic synthesis, e.g., in the syntheses of vitamins [1–3]. Rapidly growing applications of lithium metal are in lithium batteries, as the alloying component in aluminum or manganese alloys, as reducing agents for metal productions, deoxidizing and desulfurizing agents and in production of tritium in the nuclear industry as heat-exchange cooling medium and for neutron capture. Recently, lithium is largely used for lithium secondary batteries and in a heat-exchange cooling medium for a refrigerator [9–12]. Further, lithium batteries using a C_{60} compound have been developed in the State of Arizona [13].

3.3 PREPARATIONS OF ORGANOLITHIUM COMPOUNDS

Organolithium compounds are prepared mainly by the following four kinds of reactions:

(1) Direct reactions
(2) Transmetalations
(3) Metalations
(4) Hydrogen-metal exchange reactions

Firstly, organolithium compounds are prepared by the reactions of hydrocarbon halides with lithium metal as shown in eq. 3.1 [3]. This direct reaction method of preparing organolithium compounds is commonly used in commercial processes.

$$\mathrm{RX} + \mathrm{Li} \longrightarrow \mathrm{RLi} \qquad (3.1)$$

The organolithium compounds formed by the reaction shown in eq. (3.1) tend to react with hydrocarbon halides by the Wurts coupling reaction and the yields of organolithium compounds are low if the resultant organolithium compounds are very reactive compounds such as allylithium or benzyllithium. Hence, for these reactions, transmetalation reactions, as described below are used. Therefore, this reaction is used for production of organolithium compounds having relatively low reactivity such as alkyllithiums, vinyllithiums and aryllithiums [14–20].

n-Butyllithium is the most important organolithium compound which is produced by the reaction of *n*-butyl chloride with lithium metal in *n*-heptane or cyclohexane as shown in eq. (3.2). In this reaction, the yield is low when the lithium metal is of a high purity. Ordinary lithium contains a small amount of sodium, and the sodium acts as both a reaction initiator and a reaction improver. Hence, lithium containing 0.5–2 % sodium is used in the reaction shown in eq. (3.2) [21].

$$n\text{-BuCl} + \underset{(0.8\%\ \text{Na})}{2\,\text{Li}} \xrightarrow[\text{in } n\text{-heptane}]{\text{room temp, 3 h}} \underset{\text{Yield } 79.2-81.3\%}{n\text{-BuLi}} + \text{LiCl} \qquad (3.2)$$

In these direct reactions of metals such as lithium, magnesium, sodium, potassium and zinc, using sonochemistry, in which the surface of the metal is activated by irradiation by ultrasonic waves, has recently been performed [22,23]. For example, *n*-PBr [24], *n*-BuBr [25] or PhBr [25] reacts with lithium metal in an ether type solvent (ethyl ether or THF) at −10 or −60 °C for 90 or 180 min in the absence of ultrasonic waves and the yields of *n*-PrLi, *n*-BuLi and PhLi are 78, 56 and 92 %, respectively. However, in the reactions under ultrasonic waves used for 10–30 min, the yields are 90 %, 61 % and 95 %, respectively as shown in eq. (3.3) [23].

$$\text{RBr} + 2\,\text{Li} \xrightarrow[\text{in ether}]{\text{Ultrasonic Irradiation, 60W, 50 kHz}} \text{RLi} + \text{LiBr} \qquad (3.3)$$

$$\begin{array}{lccc} \text{R:} & \text{n-Pr}, & \text{n-Bu}, & \text{Ph} \\ \text{Yield:} & 90\%, & 61\%, & 95\% \end{array}$$

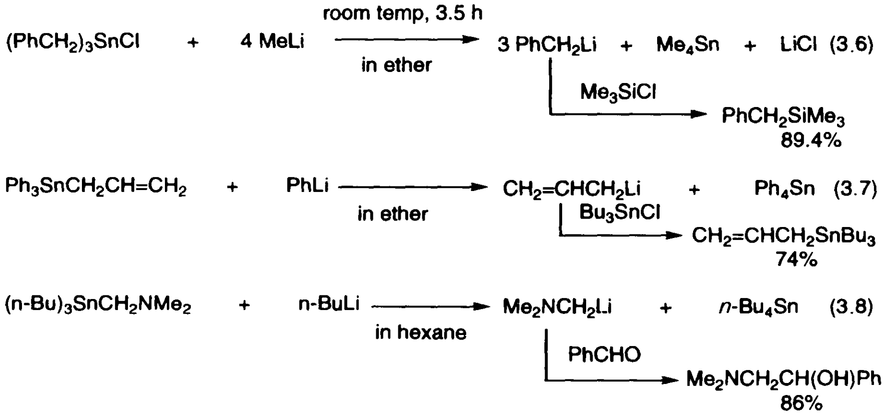
Secondly the transmetalations are a set of the two kinds of reactions shown in eqs. (3.4) and (3.5) [14]. These reactions are suitable for the syntheses of allyl, benzyl or compounds having the other kinds of functional groups on which the above direct reactions are difficult to apply. The electronegativity of the metals is required to be higher than that of lithium, and tin is frequently used.

$$\text{RM} + \text{Li} \longrightarrow \text{RLi} + \text{M} \qquad (3.4)$$

$$\text{RM} + \text{R'Li} \longrightarrow \text{RLi} + \text{R'M} \qquad (3.5)$$

M = more electronegative metal,
e.g., Hg, Si, Sn, Pb, Sb, Bi, Cd, Zn, B, Se or Te

In the reaction shown in eq. (3.5), the organic group R of an organolithium formed should have a lower acidity than that of the organic group (R′) of the compound used as a raw material. For example, the method for the syntheses of those organolithium compounds which are stabilized by a double bond or hetero atom, etc., are as shown in eqs. (3.6)–(3.8) [26–28].



$$(PhCH_2)_3SnCl + 4\,MeLi \xrightarrow[\text{in ether}]{\text{room temp, 3.5 h}} 3\,PhCH_2Li + Me_4Sn + LiCl \quad (3.6)$$

$$PhCH_2Li \xrightarrow{Me_3SiCl} PhCH_2SiMe_3 \quad 89.4\%$$

$$Ph_3SnCH_2CH{=}CH_2 + PhLi \xrightarrow[\text{in ether}]{} CH_2{=}CHCH_2Li + Ph_4Sn \quad (3.7)$$

$$CH_2{=}CHCH_2Li \xrightarrow{Bu_3SnCl} CH_2{=}CHCH_2SnBu_3 \quad 74\%$$

$$(n\text{-}Bu)_3SnCH_2NMe_2 + n\text{-}BuLi \xrightarrow[\text{in hexane}]{} Me_2NCH_2Li + n\text{-}Bu_4Sn \quad (3.8)$$

$$Me_2NCH_2Li \xrightarrow{PhCHO} Me_2NCH_2CH(OH)Ph \quad 86\%$$

Thirdly, metalations are hydrogen–metal exchange reactions as shown in eqs. (3.9) and (3.10). In organic compounds having a high acidity hydrogen atom, the hydrogen are extracted as a proton by a strong basic lithium atom, and the organolithium compounds are produced. In the case of eq. (3.9), the pKa value of RH is required to be sufficiently lower than the pKa of R'H which is produced by the reaction.

$$RH + R'Li \longrightarrow RLi + R'H \quad (3.9)$$

$$RH + LiNR'_2 \longrightarrow RLi + HNR'_2 \quad (3.10)$$

pKa values are shown in Table 3.2. In the reaction shown in eq. (3.9), in general, the reactions proceed easily if the pKa values of the organic compounds are about forty or less, and the reaction is faster if the pKa value is lower. The order of the reactivity on organolithium compounds is as follows:

$$t\text{-BuLi} > s\text{-BuLi} > n\text{-BuLi} > \text{PhLi}$$

This order is easily understandable from the data in Table 3.2 [17].

In the reaction shown in eq. (3.10), as the reactivity of the lithium amide is lower than that of alkylithium, the pKa value of the organic group of 30 or less may be used [14,17].

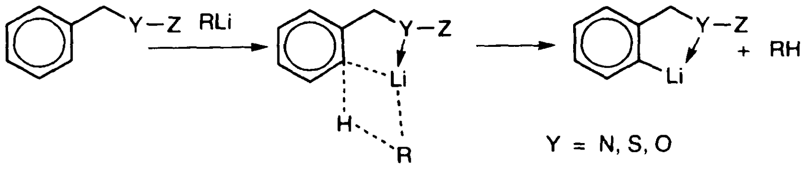
The Lewis bases, such as ether or amines, are preferably used as a solvent for the reaction shown in eq. (3.9). This is because organolithium compounds have high associative properties and they form the polymeric aggregate $(RLi)_n$ as described below. These solvents can reduce the associative properties and increase the basicity of lithium atom. For example, *n*-BuLi is a hexamer in hexane, a tetramer

Table 3.2 pKa values for organic compounds [14,17]

Compound	pKa
Me_3CH	47
Me_3CH_2	44
$Me{-}CH_3$	42
CH_4	40
cyclopropane	39.5
Ph−H	39
$H_2C{=}CH_2$	38.5
$Ph{-}CH_3$	37
$H_2C{=}CH{-}CH_3$	36.5
Ph_2CH_2	33.5
Ph_3CH	32
Cl_3CH	25
$EtOOC{-}CH_3$	24–25
$HC{\equiv}CH$	24
fluorene (9-position)	23
CH_3COCH_3	20
indene	18.5
cyclopentadiene	15
$(NC)_2CH_2$	11
O_2NCH_3	10
HCN	9
$(O_2N)_2CH_2$	3.6
$(O_2N)_3CH$	0

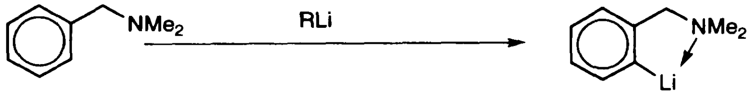
in ether and monomer in TMEDA (tetramethylene ethylenediamine, $Me_2NCH_2CH_2NMe_2$) [19]. As these solvents have a reactivity to organolithium compound in themselves, they are not suitable for reactions with a long reaction time and for storage [14,19,29].

As shown in eq. (3.11), if a hetero atom such as nitrogen, sulfur or oxygen is located at the β-position of the aromatic ring, the lithium metal at first is coordinated by the hetero atom and activated, and then it forms a stable five-membered ring by electrophilic attack at the ortho carbon. The five-membered ring formation reaction as shown in eq. (3.11), proceeds easily not only with lithium but also with the many other metals. This reaction is called orthometalation or cyclometalation [30]. For example, the five-membered ring compounds are produced by reaction of dimethylaminomethybenzene with alkyllithium as shown in eq. (3.12) [31–33]. Similar reactions are known on the compounds of metals such as Si, Sn, Hg, Mn, Cu, Ni, Cr, Co, Pt, Pd, Rh, Ti, V, Sc, Y, La, Nd and Er. [30].



Y = N, S, O

(3.11

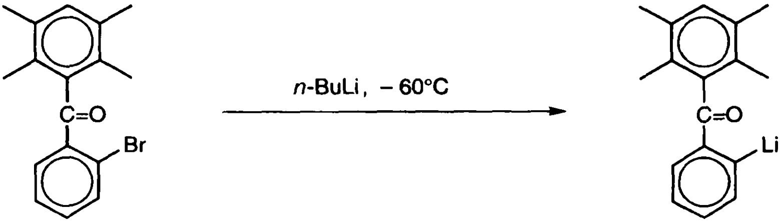


(3.12)

Fourthly the halogen–metal exchange reactions are the reactions in which halides react with organolithium as shown in eq. (3.13). The lithium atom is able to react accordingly with the relative difference in the basicity of R and R′. RH is preferred to have the smaller pKa and the stronger acidity. On the other hand, organolithium is preferred to have a larger pKa than R′H, for example, alkyllithium. Since the order of reactivity in halogens is $I \approx Br > Cl > F$, bromides are mainly obtainable.

$$\mathrm{RX} + \mathrm{R'Li} \rightleftarrows \mathrm{RLi} + \mathrm{R'X} \quad (3.13)$$

With organolithium compounds, their substitution reactions proceed without affecting the carbonyl groups as shown in eq. (3.14), and in this regard they are different from Grignard reactions [34].



(3.14)

Gschewend and Rodriguez have shown many reactions forming the five-membered ring of organolithium compounds in *Organic Reaction* vol. 26 [35]. These reactions can be considered to proceed easily and quantitatively. These ring structures supposed to be present as the intermediates are shown in Figure 3.1 [35].

3.4 STRUCTURES OF ORGANOLITHIUM COMPOUNDS

Organometallic compounds of small atomic number metals (Be, Mg, B and Al) tend to form an electron-deficient bond, and similarly organolithium compounds also tend to form an electron-deficient bond. In particular, alkyllithium forms mainly a tetramer or hexamer in solid, liquid and gas state [14,36–42].

For example, MeLi forms a distorted cubic structure of the tetramer of Li_4C_4 skeleton as shown in Figure 3.2. MeLi forms a multicenter bond; one lithium bonds with three lithium atoms and three carbon atoms, and one carbon bonds with three lithium atoms. These multicenter bonds have ionic bond properties [37–41].

The compounds having a distorted cubic Li_4C_4 skeleton are $[o\text{-Li-}C_4H_4\text{-}CH_2NMe_2]_4$ (Figure 3.3), $(PhC{\equiv}CLi)_4{\cdot}(TMPDA)_2$ (TMPDA = *N*,*N*,*N*′,*N*′-tetra-

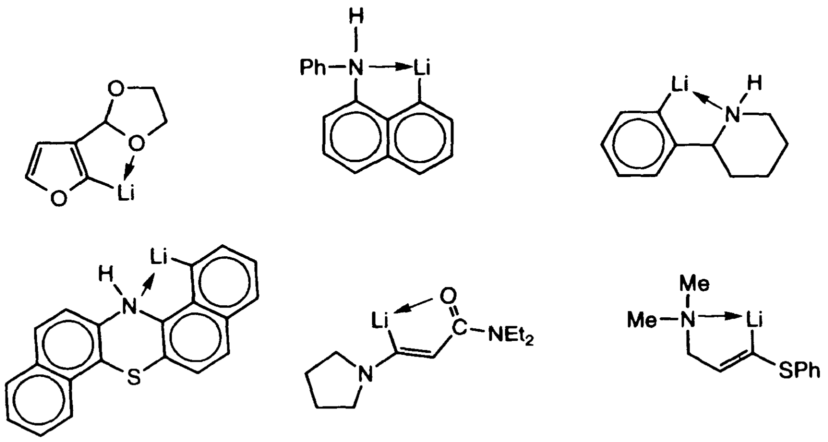
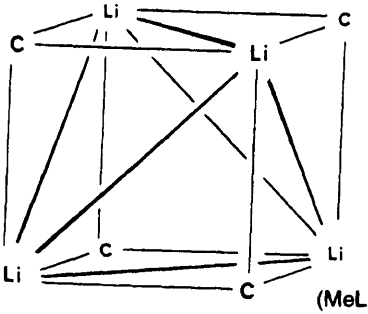


Figure 3.1 Some representative structures of organolithium compounds with five-membered ring structures [35].



	$(MeLi)_4$	$(EtLi)_4$
Li - Li	2.68 Å	2.42, 2.60, 2.63 Å
Li - C	2.31 Å	2.19, 2.25, 2.47 Å

Figure 3.2 Unit cell in the organolithium compounds with lithium tetrahedra [37–41].

methyl-1,3-propanediamine), $(PhC{\equiv}CLi)_4{\cdot}(THF)_4$, $(EtLi)_4$, etc., besides $(MeLi)_4$. In the case of $(EtLi)_4$ the distortion of cubic structure is larger compared with that of $(MeLi)_4$ because the size of alkyl group is larger by one carbon atom [37]. The crystal structure of the reaction product ($2\text{-}MeNCH_2C_6H_4Li$) in the reaction shown in eq. (3.12), is shown in Figure 3.3. The five-membered ring in this compound is not a simple coordination structure but the carbon atom in the ortho position and the lithium atom form an electron-deficient multicenter bond as shown in Figure 3.3 [33]. However, with the THF solution having a high electron-donating property, one lithium metal is coordinated by two oxygen atoms from two THF molecules and the five-membered ring structure is ruptured [43].

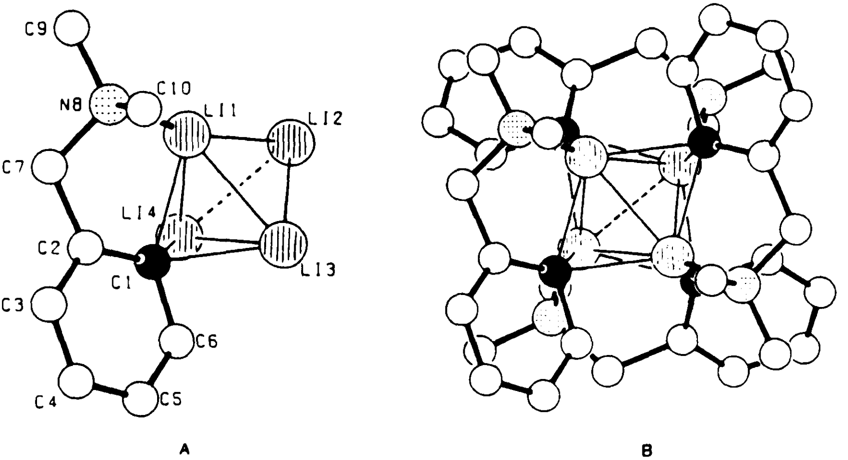


Figure 3.3 (A) Bonding of the 2-$Me_2NCH_2C_6H_4$ groups to the Li_4 tetrahedron, (B) overall structure of the Ar_4Li_4 cluster [33].

The dissociation energy of alkyllithium is very large. In the case of MeLi (dimer, trimer and tetramer) they are −42, −82 and −128 kcal/mole, respectively [42]. Organolithium compounds are non-transition metal compounds but they can form π-bond structures. The elements of non-transition metal compounds which can form the π-bond, are Na, Be, Mg, Ca, B, Al, Ga, In, Tl, Ge, Sn, Pb, P, As, Sb, S, Se, Te, etc., besides Li [44]. The olefinic π-bond with transition metals is well-known; the coordination of the π-bond is such that the electrons of the olefinic π-bond are donated to the vacant d orbitals, and the backdonation of the π-bond is such that the electrons of the metal d-orbitals are donated to the antibonding π^* orbital of the olefin. However, as non-transition metals have no vacant d orbitals, the π-electrons of olefins only partially move to the s- or p-orbital of the metal. Then, the electrons largely remain in a non-bonding orbital, and the backdonation is therefore almost none [44].

Organolithium compounds having a π-bond are known in the bonding of allyl, cyclobutadiene, cyclopentadiene and benzene ring, etc. [44–48]. For example, the π-complex of cyclopentadiene is shown in Figure 3.4 [4–7]. It is considered that this multicenter covalent bonding involving lithium may make a minor contribution but ionic interactions dominate [39,44]. The lithium atom of the cyclopentadiene π-complex, as shown in Figure 3.4, is formed by the coordination of, in total, nine electrons with five electrons from the cyclopentadienyl ring and four electrons from two nitrogen atoms. However, the octet rule consideration is not significant in lithium chemistry [39].

A lithium atom is able to form a lithocene bonding with two cyclopentadienyl rings. The lithium atom of the lithocene is anionic. For example, an anionic sandwich complex is formed as shown in eq. (3.14a). The two cyclopentadienyl

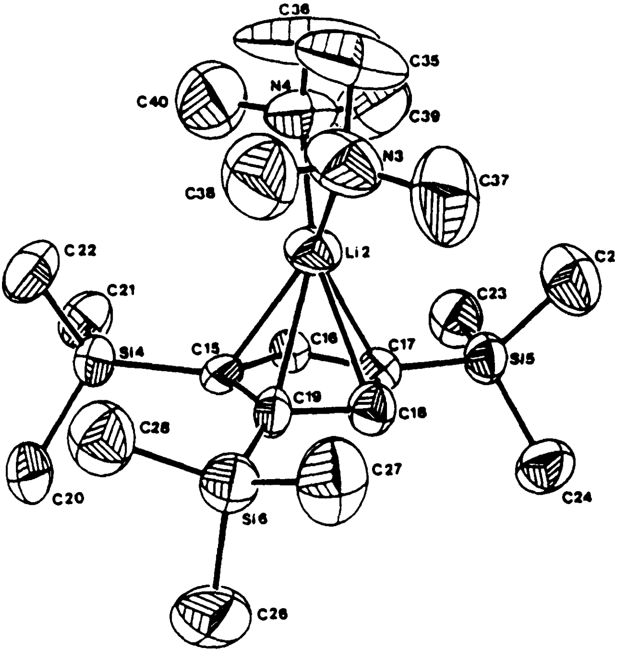


Figure 3.4 Pentagonal-pyramidal structure of tris(trimethylsilyl)cyclopentadienyl tetramethyleneethylenediamine complex [47].

rings are perfectly planar. The cyclopentadienyl rings in the anion are staggered, of a centrosymmetric nature [48a].

$$2CpLi + Ph_4PCl \xrightarrow[\text{in THF}]{} [Ph_4P]^+[Cp_2Li]^- \qquad (3\text{-}14a)$$

3.5 PROPERTIES OF ORGANOLITHIUM COMPOUNDS

Organolithium compounds as described above have a high ability of association and tend to form polymeric structures. The ability of association decreases in alkyllithiums when the alkyl group is higher. The organolithium compounds having lower alkyl groups generally show a high ability of association, a low volatility and a low solubility.

Although organolithium compounds have the smallest ionic character (Li-C 43%, Na-C 47%, K-C 52%, Rb-C 52% and Cs-C 57%) in the organoalkali compounds [15], they have a larger ionic character within the whole organometallic compounds, and their multicenter bonds and π-bonds show a larger ionic character. Therefore, organolithium compounds tend to form complexes with an electron-donating compound, for example, $MeLi \leftarrow BMe_3$. Organolithium compounds generally ignite spontaneously in the pure state or in a solution on exposure to air.

Organolithium compounds are very reactive to oxidizing gases (e.g. Cl_2), water, alcohols, phenols and acids, etc. They react with carbon dioxide, similar to Grignard reagents, to give the carboxylic acid. The reactivity of organolithium compounds, in some cases, is higher than the Grignard reagent. For example, PhLi is more reactive by around 100 times than PhMgBr in the same reaction system [15].

3.6 REACTION OF ORGANOLITHIUM COMPOUNDS

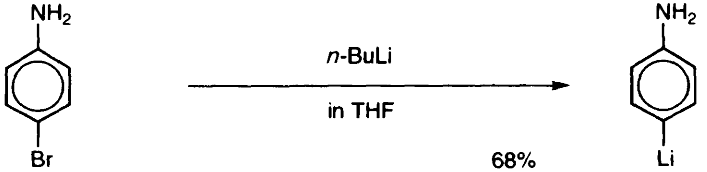
The reactions of organolithium compounds proceed similar to those of the Grignard reactions. However, organolithium compounds are used especially for the following three reactions in which the reactivities of Grignard reagents are low, as described above.

(1) Substitution reaction
(2) Addition reaction to carbon–carbon double bonds
(3) Metalation

Furthermore, organolithium compounds are also used for (4) 'transmetalation' because they are more reactive than the other organometallic compounds, (5) 'the reaction with ate complexes', because the specific reactions with ate complexes of organolithium compounds tend to easily proceed, (6) 'sonochemistry', etc.

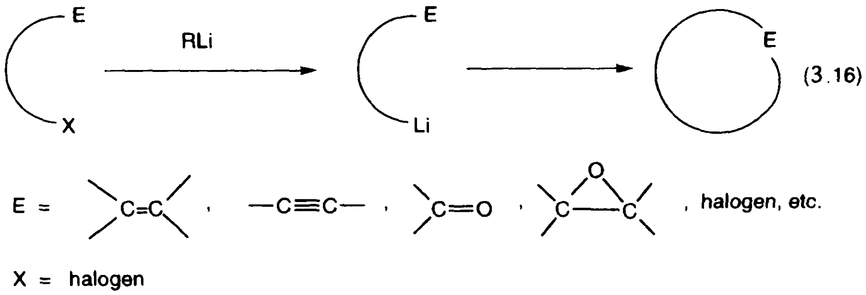
3.6.1 SUBSTITUTION REACTION

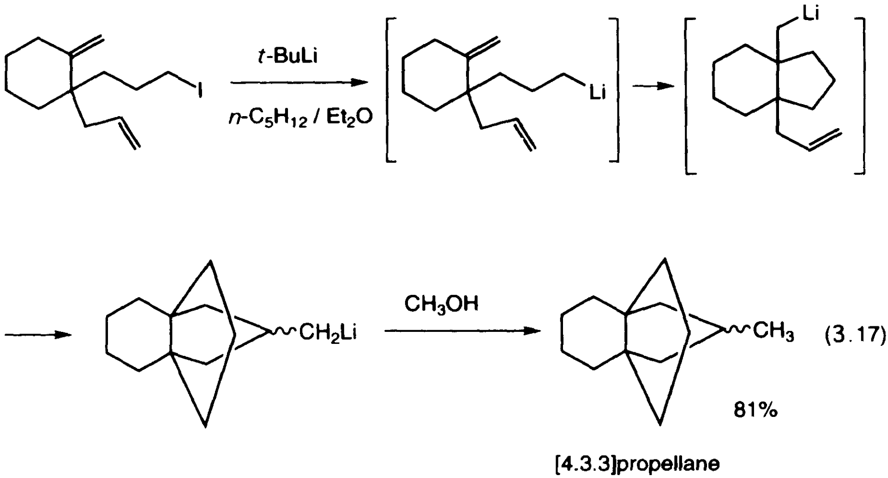
Organolithium compounds are able to substitute a halogen atom selectively without being influenced by the functional groups such as carbonyl group (eq. (3.14)) and amino group (eq. (3.15)) [49], unlike Grignard reagents. As shown in eqs. (3.14) and (3.15), the substitutions of aromatic bromides have been reported [50–52]. In the reaction of bromobenzene with *n*-butylithium in a hexane solution, the exchange is first order in bromobenzene and first order in *n*-butyllithium, with an activation energy of 12 kcal mol^{-1} (52 kJ mol^{-1}). This reaction is due to the exchange being either with a four-centered structure or an S_N2-type attack of the *n*-butyl anion at the bromine of the aryl bromide [53,54].



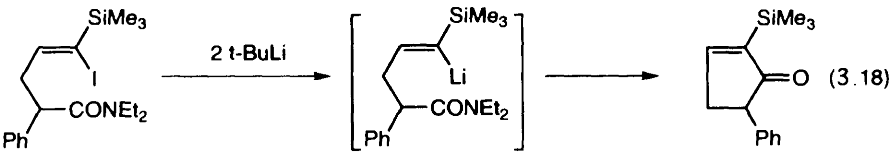
(3.15)

Intramolecular cyclization reactions proceed by reaction of halides with organolithium compounds as shown in eq. (3.16) [55], where E is a double bond, triple bond, carbonyl group, an oxyrane ring, etc. For example, as shown in eq. (3.17), an iodide having two double bonds reacts with *t*-butyllithium. The lithium adds to two double bonds stepwise, two five-membered rings are formed, and [4.3.3]propellanes are obtained in a high yield [56].

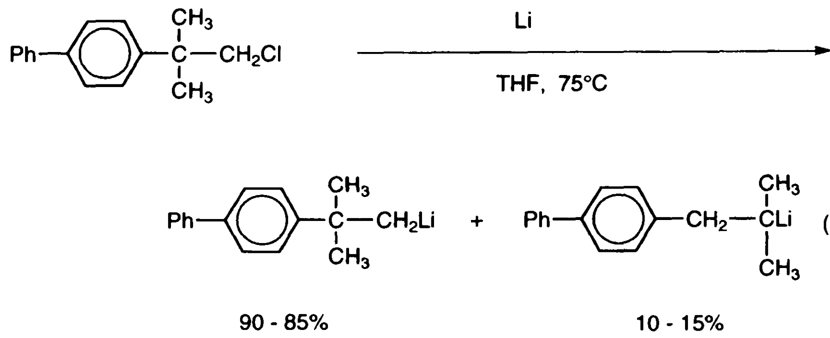




Cyclizations in which carbonyl group is an electron acceptor easily give cyclic ketones. This cyclization gives an unsaturated cyclic ketone when the raw material is a vinyl iodide as shown in eq. (3.18) [57].



In the case of haloalkylaryl compounds, the aryl migrated product of organolithium occurs when the reaction temperature is raised as shown in eq. (3.19) [58].



(3.19)

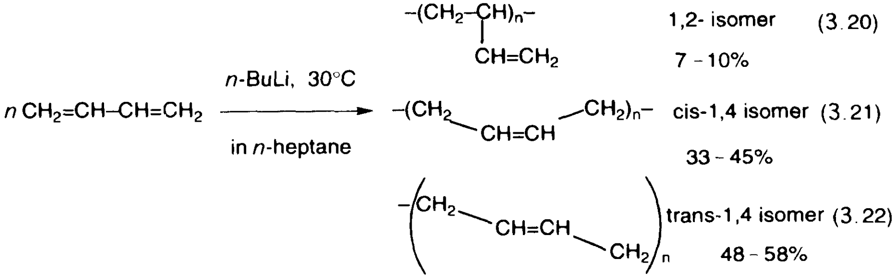
3.6.2 ADDITION REACTION TO CARBON–CARBON DOUBLE BONDS

The carbometalations of organolithium compounds to carbon–carbon double bonds have lower reactivities than those of organoboran and organoaluminum compounds but are higher than those of Grignard reagents [59]:

$$\mathrm{RMgX} < \mathrm{RLi} < \mathrm{R_3B},\ (\mathrm{R_3Al})_2$$

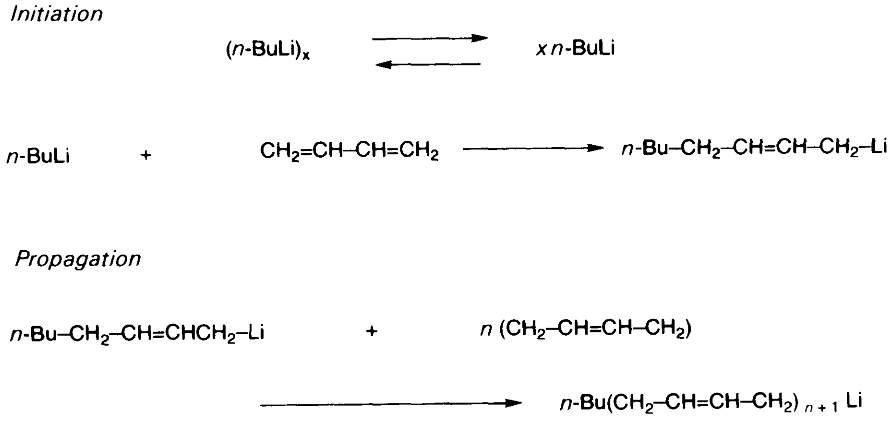
The addition reaction of organolithium compounds easily proceeds especially to intramolecular carbon–carbon double bonds (3.17) or to conjugated double bonds. The latter addition reactions proceed continuously. These reactions are utilized in butadiene and SBR polymerization and the organolithium compound is mostly used for these catalysts [60].

Butadiene is polymerized by using *n*-BuLi as shown in eqs. (3.20)–(3.22). When the ratio of the 1,2-isomer is 10 % or less, the reaction changes but the above ratio does not change when the reaction temperature (4–80 °C) or the kinds of organolithium compounds used are changed. The 1,2-isomers increase with addition of ether or amine [61,62]. Polymerization of butadiene requires high contents of *cis* and *trans* 1,4-. Thus, it is good for the reaction if the amount of the 1,2-isomer is low. In the polymerization of butadiene with organolithium compounds as the catalyst, the ratio of 1,2-isomers is lower than those with the other organoalkali compounds as the catalyst (ratio of 1,2-isomer: Na = 60 %, K = 45 %, Rb = 62 %, Cs = 59 %) [63]. Organolithium enabled the polybutadiene to be less prone to contain gel and to contain no transition metal catalyst that may be present in polybutadienes prepared with cobalt- or nickel-containing catalysts. These factors offer significant advantages in certain applications such as the impact resistance modification of plastics [63].



As shown in Scheme 3.1 [63], organolithium compounds in hydrocarbon solvent exist largely in the form of tetramers or hexamers. Initiation apparently occurs when a monomolecular species in equilibrium with the associated species adds to the 1,4- of butadiene to give an allylic lithium compound, which propagates by repeated 1,4-addition until all butadiene is consumed. The intermediate allylic lithium compounds are stable enough to remain active at room temperature almost indefinitely [63].

The allyllithiums which are formed by addition of organolithiums add to butadiene, and tend to copolymerize with monomers such as styrene to give the block copolymers by forming the stable living polymers. Styrene polymerizes more easily than butadiene (the homopolymerization of styrene by *n*-butyllithium in *n*-heptane at 30 °C is approximately six times faster than the homopolymerization of butadiene under the same condition [64]). However, in copolymerization of a mixture of the two monomers, butadiene is the more reactive comonomer. When 90 % of the butadiene monomer has been converted to polymer, more than 80 % of the styrene monomer present at the beginning of the reaction still remains. When the butadiene has all reacted a marked increase in the polymerization rate of styrene

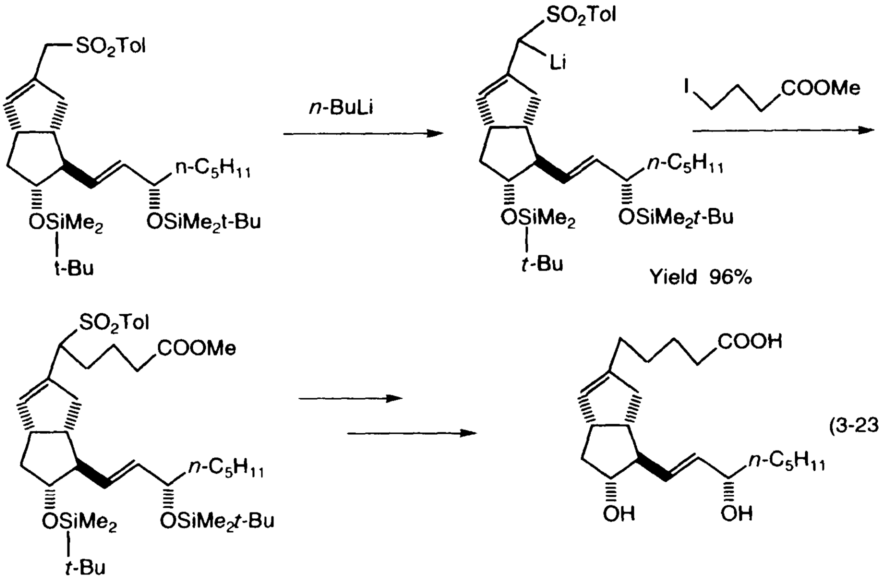


Scheme 3.1 [63]

is observed. Hence, in copolymerization of butadiene and styrene, at first butadiene polymerizes in the presence of a small amount of styrene, and then styrene adds to easily give a block copolymerization product [63–65]. *n*-Butyllithium is widely used for the catalysts of industrial production of SBR.

3.6.3 METALATION

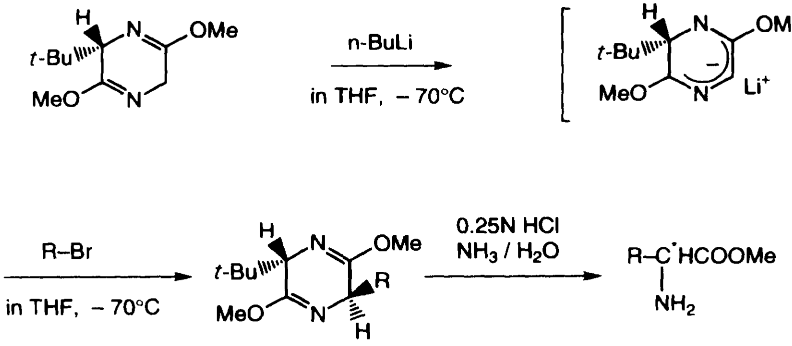
Grignard reagents are able to metalate only reactive hydrocarbon such as acetylenes, but with organolithium compounds the metalation proceeds when the pKa of the substrate is 40 or less as shown in eq. (3.9). Therefore, the metalation with organolithium compounds is used for organosynthetic reaction together with substitution of halides, especially for syntheses of pharmaceuticals, agrochemicals and perfumes. For example, isocarbacyclins are a stable prostacyclin analogue having blood platelet agglutination inhibition, the dissociation of aggregates and blood vessel smooth muscle relaxation. The isocarbacyclins have physiological activities similar to PGI_2 and are more stable than PGI_2. In the synthetic reaction for these intermediates *n*-butyllithium is used for the metalation reaction as shown in eq. (3.23) [66].



(3-23)

Isocarbacyclin

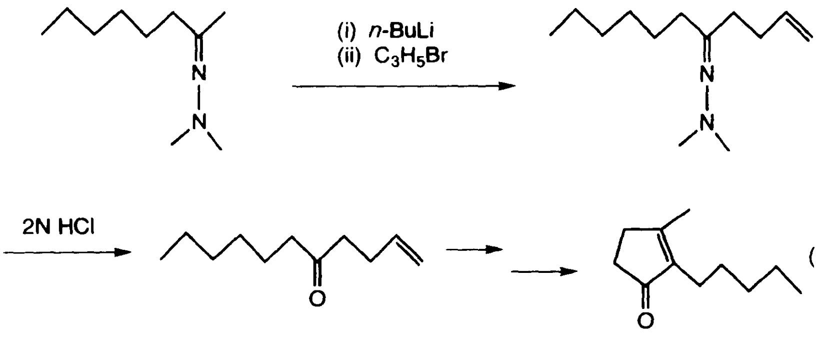
Since 6-methylene of 3,6-dihydroxypyrazines is reactive, it easily gives the substituted products with the bromides after the reaction with organolithium compounds, as shown in eq. (3.24). If the substituents of dihydroxypyrazines are optically active, optically active amino acids are prepared by the asymmetric reaction [67–72].



(3.24)

R = $PhCH_2$ Yield 76%, >95% ee
R = $-CH_2CH{=}CH_2$ Yield 87%, 94% ee

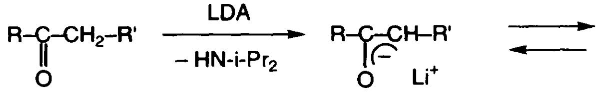
The terminal methyl group of unsymmetrical ketone dimethylhydrazone is reactive, and is easily metalated with organolithium compounds. Subsequently, the substituted products are produced by reaction with halides as shown in eq. (3.25). These reactions are applied for the synthesis of dihydrojasmone [73].



(3.25)

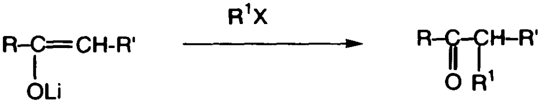
dihydrojasmone

As described in the reaction shown in eq. (3.10), with a compound of pKa 30 or less the lithiation is carried out with lithium amide, in particular with lithium isopropylamide (LDA). For example, the carbonyl compounds having a α-proton react with LDA to give the conjugate lithium enolates as shown in eq. (3.26). The lithium enolates easily couple with halides to give α-substituted products as shown in eq. (3.27). Further, aldol adducts are yielded with ketones or aldehydes as shown in eq. (3.28) [19].



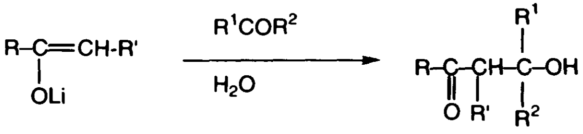
$$\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2{-}R'} \xrightarrow[-\ \mathrm{HN\text{-}i\text{-}Pr_2}]{\mathrm{LDA}} \mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{-}{C}H{-}R'\ Li^+} \rightleftarrows \mathrm{R{-}\underset{\displaystyle OLi}{\underset{|}{C}}{=}CH{-}R'} \quad (3.26)$$

LDA (Lithium diisopropylamide) = LiN-i-Pr_2



$$\mathrm{R{-}\underset{\displaystyle OLi}{\underset{|}{C}}{=}CH{-}R'} \xrightarrow{\mathrm{R^1X}} \mathrm{R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle R^1}{\underset{|}{C}}H{-}R'}$$

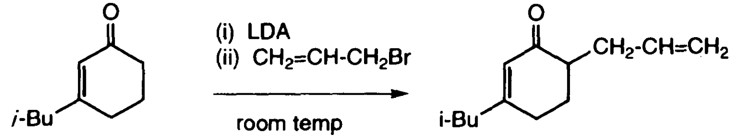
coupling reaction (3.27)



$$\mathrm{R{-}\underset{\displaystyle OLi}{\underset{|}{C}}{=}CH{-}R'} \xrightarrow[\mathrm{H_2O}]{\mathrm{R^1COR^2}} \mathrm{R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle R'}{\underset{|}{C}}H{-}\overset{\displaystyle R^1}{\overset{|}{\underset{\displaystyle R^2}{\underset{|}{C}}}}{-}OH}$$

aldol addition (3.28)

For example, β-diketone enol ethers react with LDA, and then react with allyl bromide to give allyl compounds as shown in eq. (3.29) quantitatively [74].



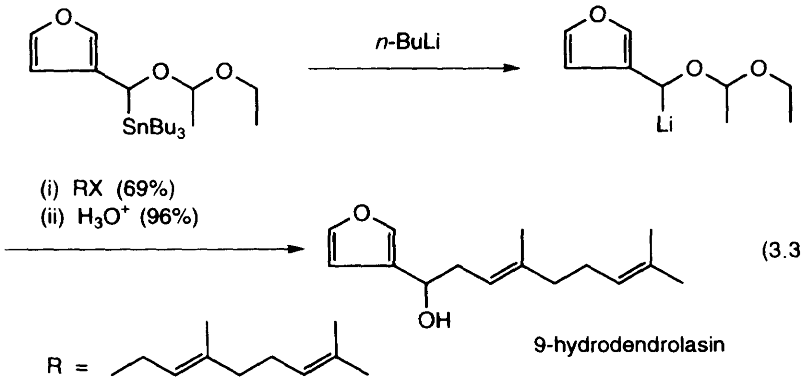
(3.29)

3.6.4 TRANSMETALATION

Transmetalation of lithium or organolithium compounds with various kinds of organometallic compounds proceeds as described above and shown in eqs. (3.4) and (3.5). In particular, the transmetalation with organotin compounds is widely utilized for organic syntheses as shown in eq. (3.30) [75–77]. The transmetalation reaction of tin and lithium as shown in eq. (3.30) is in an equilibrium state and if R is an alkenyl, an alkynyl, an allyl and substituents having a hetero atom, the reaction easily proceeds. If R is a saturated alkyl group, the reaction is difficult [75,76].

$$\mathrm{R'_3Sn{-}R} \quad + \quad n\text{-}\mathrm{BuLi} \rightleftarrows \mathrm{RLi} \quad + \quad \mathrm{R'_3Sn}{-}n\text{-}\mathrm{Bu} \qquad (3.30)$$

For example, with the organotin compound having hetero atoms the transmetalation proceeds easily by the stabilization effects of hetero atoms. Then, the lithium compounds react with alkenyl halides and are hydrolyzed to give naturally obtainable 9-hydroxydendrolasin [75].



(3.31)

3.6.5 REACTION WITH ATE COMPLEXES

Organolithium compounds react with alkylmetals or metal halides such as boron, magnesium, aluminum, copper, zinc and tellurium compounds, and the reactions give the ate complexes as shown in eqs. (3.32) and (3.33) [78].

$$\mathrm{RLi} + \mathrm{R'_3B} \longrightarrow \mathrm{Li^+[R{-}\overset{\displaystyle R'}{\underset{\displaystyle R'}{B}}{-}R']^-} \quad (3.32)$$

$$2\,\mathrm{RLi} + \mathrm{CuX} \longrightarrow \mathrm{Li^+[CuR_2]^-} + \mathrm{LiX} \quad (3.33)$$

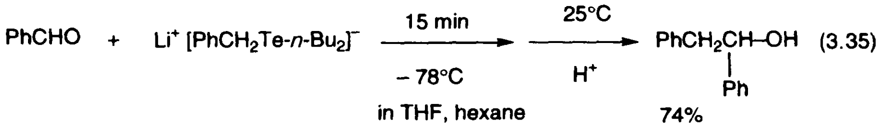
The nucleophilic reactivities of organocopper–lithium ate complexes are lower than those of either a Grignard reagent or organolithium compounds. Then they are able to add to the 1,4-position of the double bond conjugated with ketone or the other carbonyl groups [79].

The reactions of organotellurium compound with organolithium compounds give the ate complex as shown in eq. (3.34).

$$\mathrm{PhCH_2Te\text{-}}n\mathrm{\text{-}Bu} \xrightarrow[\text{in THF, }-78^\circ\text{C, 15 min}]{n\text{-BuLi}} \mathrm{Li^+[PhCH_2Te\text{-}}n\mathrm{\text{-}Bu_2]^-}$$

$$\longrightarrow [\ \mathrm{PhCH_2Li} + \mathrm{Te\text{-}}n\mathrm{\text{-}Bu_2}\ ] \quad (3.34)$$

Furthermore, aldehyde reacts with the ate complex. Then the reaction product of the aldehyde with the organolithium compound, which is produced by tellurium–lithium exchange reaction, is produced [80]. These reactions are applied for a convenient reaction with benzyllithium or allyllithium for which the usual halogen–lithium exchange reactions are difficult as shown in eq. (3.35) [80,81].



$$\mathrm{PhCHO} + \mathrm{Li^+[PhCH_2Te\text{-}\mathit{n}\text{-}Bu_2]^-} \xrightarrow[\substack{-78°\mathrm{C}\\ \text{in THF, hexane}}]{15\text{ min}} \xrightarrow[\mathrm{H^+}]{25°\mathrm{C}} \underset{\substack{|\\ \mathrm{Ph}\\ 74\%}}{\mathrm{PhCH_2CH{-}OH}} \tag{3.35}$$

3.6.6 OTHERS

The other reactions are the addition reaction of carbonyl groups [16,19], the addition reaction of carbon–nitrogen unsaturated bond, intramolecular rearrangements (3.19) [16] and the Barbier reaction of sonochemistry, etc. Here, I will describe only the Barbier reactions of sonochemistry. Recently, an ultrasonic technique has been used for dispersion, emulsification, deaeration, and washing. In 1986, this ultrasonic technique had also started to be used for organosynthetic reactions, and it was noted that the organosynthetic method simply shows short reaction time and high yields [22]. It is considered that the improvements in the reaction rate with ultrasound is caused by cavitation phenomena.

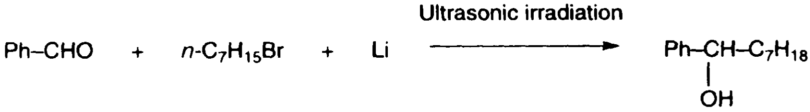
When sound waves are propagated in a liquid, they cause high pressure spots or low pressure spots to occur locally, corresponding to the sound wave shapes. The low pressure spots tear off the liquid to cavitate because the low pressure at the low pressure spots is larger than intermolecular interaction of liquid. At the next pressure cycle, the cavity is crushed and disappears. However, this time liquid molecules collide each other with an acceleration of several ten thousand times around the crushed cavity to produce several hundred atm pressure and a temperature of several thousand degree centigrade, over a short time scale 10 ns order. Under irradiation of ultrasound, these cycles are repeated several ten thousand times per second [22]. These cavitation effects tend to occur at 20–100 kHz.

In general, in the reaction of benzyl halide with lithium, the yield of benzyllithium is low since the Wurts coupling reaction proceeds. However, with the addition of ketones to this reaction system and ultrasound irradiation, Barbier reaction then proceeds. It is believed that this reaction yields benzyllithium as an intermediate and the benzyllithium reacts with ketone [23].

The Grignard reaction is carried out by two-step reactions. First is the formation reaction of the Grignard reagent and the second is the Grignard reaction. However, the Barbier reaction as shown in eq. (3.36), is carried out in a one-step reaction [82,83].

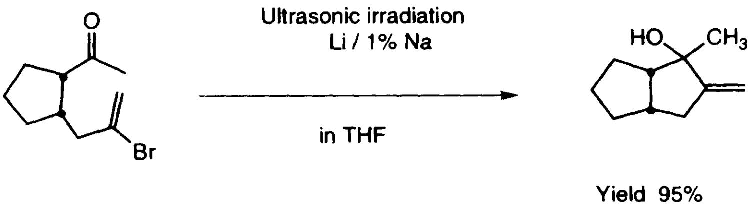
$$\mathrm{PhCH_2Br} + \mathrm{CH_3COCH_3} \xrightarrow[\substack{\text{in THF}\\ 60\text{ W, }50\text{ kHz}}]{\substack{\text{Ultrasonic irradiation}\\ 30\text{ min, room temp}\\ \text{Li-2\% Na}}} \underset{\text{yield }100\%}{\mathrm{Ph{-}CH_2C(CH_3)_2OH}} \tag{3.36}$$

Lithium or zinc, besides magnesium as the metal atom, can be used as shown in eq. (3.36). The Barbier reaction with lithium is usually carried out under an inert gas atmosphere, at room temperature or below, for about two hours. The yield is usually 80 % or less. However, in the reactions under ultrasonic irradiation, the yields are improved as shown in eq. (3.36). For example, benzaldehyde reacts with *n*-heptylbromide under ultrasonic irradiation for only ten minutes to give an alcohol in 94 % yield as shown in eq. (3.37) [84].



$$\text{Ph–CHO} + n\text{-C}_7\text{H}_{15}\text{Br} + \text{Li} \xrightarrow{\text{Ultrasonic irradiation}} \underset{\text{OH}}{\underset{|}{\text{Ph–CH}}}\text{–C}_7\text{H}_{18} \qquad (3.37)$$

On the other hand, the reaction of the compound having halogen and a carbonyl group with lithium–metal under ultrasonic irradiation gives a cyclization product in high yield as shown in eq. (3.38) [85].



(3.38)

REFERENCES

[1] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd. ed. John Wiley, New York, vol. 14, p. 448, 1980.

[2] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 4th. ed. John Wiley, New York, vol. 15, p. 393, 1995.

[3] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol. A15, p. 393, 1990.

[4] *12695 no Kagaku Shohin*, Kagaku Kogyu Nipposha, Tokyo, 1995.

[5] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.

[6] *Kagaku Binran Ooyohen*, Japan Chemical Society, Maruzen, Tokyo, p. 298, 1980.

[7] *11892 no Kagaku Shohin*, Kagaku Kogyo Nipposha, p. 186, 1992.

[8] *Kagaku Kogyo Jiho*, June 5, 1992.

[9] *Kagaku Kogyo Jiho*, December 15, 1994.

[10] M. Wakihara, *Kino Zairyo*, 14, June (1994) 5.

[11] *Kagaku Kogyo Jiho*, November 25, 1994.

[12] *Kino Zairyo*, 14, Oct (1994) 63.

[13] *Kagaku Kogyo Jiho*, September 5, 1994.

[14] J.L. Wardell, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 1, p. 43, 1982.

[15] E.G. Rochow, D.T. Hurd and R.N. Lewis, *Chemistry of Organometallic Compounds*, John Wiley, New York, p. 65, 1957.

[16] Kinki Kagaku Kogyokai, *Yukikizoku Kagaku to Ooyo*, Asakura Shoten, p. 134, 1962. G.E. Coats, *Organo-Metallic Compounds*, Methuen, London, 1960.

[17] Y. Yamamoto and Y. Naruta, *Yuki Kinzoku Kagaku (Organometallic Chemistry)*, Maruzen, Tokyo, p. 4, 1983.
A. Streitwieser, Jr. and C.H. Heathcock, *Introduction to Organic Chemistry*, Macmillan, New York, p. 1279, 1976.

[18] A. Yamamoto, *Yukikinzoku Kagobutsu, Gosei oyobi Riyoho*, Tokyo Kagaku Dojin, Tokyo, p. 38, 1991.

[19] H. Yamazaki and Y. Wakatsuki, *Yuki Kinzoku no Kagaku (Organometallic Chemistry)*, Japan Chemical Society, Dai Nippon Tosho, Tokyo, p. 50, 1989.

[20] J.H. Harwood, *Industrial Applications of the Organometallic Compounds*, Chapman & Hall, London, p. 5, 1963.

[21] J.A. Beel, W.G. Koch, G.E. Tomasi, D.E. Hermansen and P. Fleetwood, *J. Org. Chem.*, **24** (1959) 2036.

[22] T. Kimura and T. Ando, *Yuki Gosei Kagaku Kyokaishi*, **46** (1988) 1124.

[23] J.-L. Luche and J.-C. Damiano, *J. Am. Chem. Soc.*, **102** (1980) 7926.

[24] H. Gilman, J.A. Beel, C.G. Brannen, M.W. Bullock, G.E. Dunn and L.S. Miller, *J. Am. Chem. Soc.*, **71** (1949) 1499.

[25] H. Gilman and B.J. Gay, *J. Org. Chem.*, **22** (1957) 1165.

[26] D. Seyferth, R. Suzuki, C.J. Murphy and C.R. Sabet, *J. Organomet. Chem.*, **2** (1964) 431.

[27] D. Seyferth and M.A. Weiner, *J. Org. Chem.*, **26** (1961) 4797.

[28] D.J. Peterson, *J. Organomet. Chem.*, **21** (1970) P63.

[29] J.M. Mallan and R.L. Bebb, *Chem. Rev.*, **69** (1969) 693.

[30] I. Omae, *Organometallic Intramolecular-coordination Compounds, J. Organomet. Chem. Library 18*, Elsevier, Amsterdam, 1986.

[31] F.N. Jones and C.R. Hauser, *J. Org. Chem.*, **27** (1962) 701.

[32] W.H. Puterbaugh and C.R. Hauser, *J. Am. Chem. Soc.*, **85** (1963) 2467.

[33] J.T.B.H. Jastrzebski, G. van Koten, M. Konijn and C.H. Stam, *J. Am. Chem. Soc.*, **104** (1982) 5490.

[34] R.C. Fuson, W.C. Hammann and W.E. Smith, *J. Org. Chem*, **19** (1954) 674.

[35] H.W. Gschwend and H.R. Rodriguez, *Org. Reaction*, **26** (1979) 1.

[36] J.P. Oliver, *Adv. Organomet. Chem.*, **15** (1977) 235.

[37] T.L. Brown, *Adv. Organomet. Chem.*, **3** (1965) 365.

[38] M.E. O'Neill and K. Wade, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 1, p. 1, 1982.

[39] W.N. Setzer and P. von R. Schleyer, *Adv. Organomet Chem.*, **24** (1985) 353.

[40] E. Weiss and E.A.C. Lucken, *J. Organomet. Chem.*, **2** (1964) 197.

[41] E. Weiss and G. Hencken, *J. Organomet. Chem.*, **21** (1970) 265.

[42] P. von R. Schleyer, *Pure Appl. Chem.*, **56** (1984) 151.

[43] E. Wehman, Thesis (Cyclometallated Complexes of Lithium, Copper and Platinum), 1988.

[44] P. Jutzi, *Adv. Organomet. Chem.*, **26** (1977) 217.

[45] P. Jutzi, *Pure App.. Chem.*, **61** (1989) 1731.
C. Schade and P. von R. Schleyer, *Adv. Organomet. Chem.*, **27** (1987) 169.

[46] A. Sekiguchi, *Yuki Gosei Kagaku Kyokaishi*, **50** (1992) 225.

[47] P. Jutzi, E. Schlüter, S. Pohl and W. Saak, *Chem. Ber.*, **118** (1985) 1959.

[48] K.C. Waterman and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **106** (1984) 3138.

[48a] S. Harder and M.H. Prosenc, *Angew. Chem. Int. Ed. Engl.*, **33** (1994) 1744.

[49] R.G. Jones, *Organic Reaction*, **6** (1951) 339.

[50] B.J. Wakefield, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 7, p. 1, 1982.

[51] I.T. Millar and H. Heaney, *Quart. Rev.*, **11** (1957) 109.

[52] P. Buck and G. Köbrich, *Chem. Ber.*, **103** (1970) 1420.

[53] H.R. Rogers and J. Houk, *J. Am. Chem. Soc.*, **104** (1982) 522.

[54] W.F. Bailey and J.J. Patricia, *J. Organomet. Chem.*, **352** (1988) 1.

[55] S.Saeki, *Yuki Gosei Kagaku Kyokaishi*, **50** (1992) 213.

[56] W.F. Bailey and K. Rossi, *J. Am. Chem. Soc.*, **111** (1989) 765.

[57] H. Sawada, M. Webb, A.T. Stoll and E. Negishi, *Tetrahedron Lett.*, (1986)775.

[58] E. Grovenstein, Jr., *Adv. Organomet. Chem.*, **16** (1977) 167.

[59] C. Elschenbroich and A. Saltzer, *Organometallics*, VCH, Weinheim, p. 19, 1989.

[60] A.F. Halasa, D.N. Schulz, D.P. Tate and V.D. Mochel, *Adv Organomet. Chem.*, **18** (1980) 55.

[61] I. Kuntz and A. Gerber, *J. Polymer Sci.*, **42** (1960) 299.

[62] T.A. Antkowiak, A.E. Oberster, A.F. Halasa and D.P. Tate *A-1*, **10** (1972) 1319.

[63] *Encyclopedia of Polymer Science and Engineering*, vol. 2, John Wiley, New York, p. 537, 1989.

[64] I. Kuntz, *J. Polymer Sci.*, **54** (1961) 569.

[65] A.F. Johnson and D.J. Worsfold, *Makromol. Chem.*, **85** (1965) 273.

[66] T. Tanaka and S. Kurozumi, *Yuki Gosei Kagaku Kyokaishi*, **50** (1992) 143.

[67] K. Ogura and T. Inaba, *Yuki Gosei Kagaku Kyokaishi*, **49** (1991) 575.
S. Ikegami, T. Hayama, T. Katsuki and M. Yamaguchi, *Tetrahedron Lett.*, **27** (1986) 3403.

[68] U. Schöllkopf, U. Groth and C. Deng, *Angew. Chem. Int. Ed. Engl.*, **20** (1981) 798.

[69] U. Schöllkopf, W. Hartwig, K.-H. Pospischil and H. Kehne, *Synthesis*, (1981)966.

[70] U. Schöllkopf and H.-J. Neubauer, *Synthesis*, (1982)861.

[71] J. Nozulak and U. Schöllkopf,, *Synthesis*, (1982)866.

[72] U. Schöllkopf, J. Nozulak and U. Groth, *Synthesis*, (1982)868.

[73] M. Yamashita, K. Matsumiya, M. Tanabe and R. Suemitsu, *Bull. Chem. Soc. Japan*, **58** (1985) 407.

[74] G. Stork and R.L. Danheiser, *J. Org. Chem.*, **38** (1973) 1775.

[75] M. Yamamoto, S. Kohmoto and K. Yamada, *Yuki Gosei Kagaku Kyokaishi*, **46** (1988) 1134.

[76] T. Sato, *Synthesis*, (1990)259.

[77] M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, 1987.

[78] K. Yamakawa, Y. Matsushima and M. Hisatome, *Yukikinzoku Sakutai no Kagaku*, Kodansha, Tokyo, p. 76, 1985.

[79] E. Nakamura and M. Isaka, *Yuki Gosei Kagaku Kyokaishi*, **49** (1991) 902.
H. Gilman, R.G. Jones and L.A. Woods, *J. Organic. Chem*, **17** (1952) 1630.

[80] N. Kambe and N. Sonoda, *Kagaku to Kogyo*, **66** (1992) 38.

[81] T. Hiiro, N. Kambe, A. Ogawa, N. Miyoshi and N. Sonoda, *Angew. Chem. Int. Ed. Engl.*, **26** (1987) 1187.

[82] C. Blomberg and F.A. Hartog, *Synthesis*, (1977)18.

[83] P.J. Pearce, D.H. Richards and N.F. Scilly, *J. Chem. Soc. Perkin Trans.I*, (1972)1655.

[84] J.C. Souza-Barboza, C. Pétrier and J.-L. Luche, *J. Org. Chem.*, **53** (1988) 1212.

[85] B.M. Trost and B.P. Coppola, *J. Am. Chem. Soc.*, **104** (1982) 6879.

4 Organomagnesium Compounds

4.1 INTRODUCTION

Speaking of organomagnesium compounds, Grignard reagents are cited. The Grignard reagents were discovered in 1900 by Grignard [1,2]. Even at the present time, they are widely used as the most representative reagent for organosynthetic reactions. Grignard reagents do not show any violently ignitable property and their handling is easy though their reactivity is very high with various kinds of compounds. However, as is generally well known, there is an induction period in Grignard reactions. The reaction violently and immediately proceeds soon after the reactions start. Consequently, the control of reaction heat is difficult, especially in a large reaction vessel. But, in spite of these faults, Grignard reactions are used not only for syntheses in the laboratories, needless to say, but also for industrial production of various kinds of compounds because of their high reactivity and easy handling [3–6].

4.2 MAGNESIUM

Magnesium belongs to group 2 of the periodic table, i.e., the alkali earth metals. Magnesium is the seventh most abundant element in the Earth's crust, with the average magnesium content being 2.30 %. Sodium is the most abundant element in seawater and brines, and magnesium is the second. The content in seawater is 1.29 g/dm^3 [7]. As the amount of seawater on the Earth is $1.32 \times 10^{18} m^3$ [8], then 1.70×10^{15} ton of magnesium exists in seawater. The production of magnesium per year was 282×10^3 ton in 1994 in the world [8a,8b]. The primary raw material sources for magnesium are dolomite ($CaCO_3 \cdot MgCO_3$), magnesite ($MgCO_3$), seawater and brines [9–11]. 10^8 times or more of the world production per year of magnesium exists in seawater as the raw material source. Thus it may safely be said that there is no need to worry about the exhaustion of resources for magnesium.

Calcium hydroxide is added to seawater or brines to precipitate $Mg(OH)_2$ from $MgCl_2$. Hydrochloric acid is added to $Mg(OH)_2$, then the mixture solution is heated to cause evaporation, and $MgCl_2 \cdot 1.25H_2O$ is obtained. Magnesite ($MgCO_3$) or $Mg(OH)_2$ is burnt to give magnesia, MgO, and the resultant magnesium is burnt at 1000 °C with coal or peat in chlorine gas to yield anhydrous $MgCl_2$ [9–11].

$$MgO + C + Cl_2 \longrightarrow MgCl_2 + CO \quad (4.1)$$

Magnesium metal is produced from $MgCl_2 \cdot 1.25H_2O$ or anhydrous $MgCl_2$ by electrolysis or reduction with silicon. The IG process and Dow process are the principal industrial electrolysis processes. IG process: about 10% of anhydrous $MgCl_2$ is added to a mixture of $CaCl_2$ (40%)–KCl (20%)–$NaCl_2$ (30%) electrolytes and they are electrolyzed at 740 °C. Chlorine gas is generated on the anode and magnesium deposits on the cathode. Dow process: 23% of $MgCl_2 \cdot 1.25H_2O$ is added to a mixture of NaCl (54%)–$CaCl_2$ (23%) electrolytes and they are electrolyzed at 700 °C. The chlorine gas which is generated on the anode, is obtained as hydrochloric acid, and magnesium deposits on the cathode. The purity of the magnesium obtained by these electrolysis processes is 99.8% or more [9–12].

Reduction with silicon is carried out with silicon containing 20–25% of iron as a reducing agent. There are two processes for the reduction, i.e., the Pidgeon process and the Magnetherm process. The Pidgeon process uses calcined dolomite as raw materials. Magnesium is produced by a vacuum reductive distillation (1150–1200 °C/10^{-2} Torr) with ferrosilicon. In the Magnetherm process, the melting point of the slag is lowered by adding alumina or bauxite to the calcined dolomite. The slag is able to be removed as a fusible material from the vacuum reduction furnace. The Magnetherm process is operated continuously at 25 Torr and 1500 °C. The purity of magnesium in these processes is 99.95% or more.

$$2(MgO \cdot CaO) + Si + nAl_2O_3 \longrightarrow 2Mg + 2CaO \cdot SiO_2 \cdot nAl_2O_3 \quad (4.2)$$

70% or more of magnesium metal is used in aluminum-alloy metals. The strength and corrosion resistance of aluminum is improved by adding several percent of magnesium to it. Thus aluminum alloy is then useful for the construction of cars, buildings, ships and aircraft [9]. Magnesium alloys composed mainly of magnesium are light and their strength is high. They are used for aircraft, OA machineries and optical instruments, etc. Mg–Y–Nd alloy has a high strength at 200–300 °C. The specific gravity of the alloy containing lithium metal is 1.5 or less. It is the lightest of the useful metals [12a]. Magnesium metal is exploited as reducing agents for the production of titanium or zirconium, desulfurizing agents for iron and steel, the raw materials of fireworks, flare (light bomb), photoflash lamp, and Grignard reagents [5,9].

The physical properties of magnesium are shown in Table 4.1 [11,13,13a]. Magnesium is a silver white metal, and is the lightest in the metals for structural uses. The specific gravity is only 1.738. The mechanical strength is low, but the specific strength is high because it is light.

Magnesium is insoluble in an aqueous alkaline solution and it is also stable in air at ordinary temperatures because of the formation of an oxide layer. It burns violently at a high temperature to give MgO, is spoiled by acids or salts, generates hydrogen by reaction with hot water or an acid, and occasionally the generated

Table 4.1 Physical properties of magnesium [11,13,13a]

properties	value
melting point, °C	650
boiling point, °C	1103
density at 20 °C, g/cm^3	1.738
crystal structure	closed-packed hexagonal
electrical resistivity at 20 °C, μΩ·cm	4.45
thermal conductivity at 25 °C, W/(m·K)	155
heat of fusion at 20 °C, kJ/kg	386
heat of sublimation at 20 °C, kJ/kg	6109
specific heat at 20 °C, J/(kg·K)	1025
surface tension at 20 °C, mN/m (= dyn/cm)	563
linear coefficient of thermal expansion at 20 °C	$25.2 \times 10^{-6}\text{K}^{-1}$

hydrogen detonates. Magnesium reacts with halogen to give MgX_2 and at a high temperature reacts with nitrogen to give Mg_3N_2 [9–14].

4.3 PREPARATION OF ORGANOMAGNESIUM COMPOUNDS

Generally the organomagnesium compounds are mostly used as Grignard reagents (RMgX) for synthetic reactions. The other known organomagnesium compounds are R_2Mg, RMgH, RMgOR′, RMgSR′, RMgNRR′, $MMgR_3$ (M = Li, Na, K, Rb, Cs), $[R_2Mg{\cdot}R'_3Al]_2$, etc. These are also prepared from mainly Grignard reagents [15,16].

4.3.1 GRIGNARD REAGENTS

Grignard reagents are primarily synthesized by reaction of magnesium with organic halides in either a diethyl ether (Et_2O) or tetrahydrofuran solvent.

$$\mathrm{RX} + \mathrm{Mg} \xrightarrow[\text{in ether or THF}]{} \mathrm{RMgX} \qquad (4.3)$$

The Grignard reaction is a reaction which anyone who performs organic syntheses, experiences at least one time. It is well known how the reaction should be performed, for example, solvents and alkyl halides as the raw materials should be dried thoroughly, and a new surface of magnesium should be exposed by cutting with scissors just before the reaction starts because magnesium tends to be covered with a protective oxide surface.

If the reaction does not proceed because the reaction requires highly reactive magnesium, it should be powdered in an inert gas atmosphere with a powdering machine. The most reactive magnesium is produced by the Rieke method [17–21]. This magnesium is obtained by reduction of magnesium chloride with potassium, lithium or sodium in tetrahydrofuran. It is ignitable and is able to be used for fluorides and bis Grignard reagents (e.g. $BrMg(CH_2)_nMgBr$) which do not proceed in ordinary reaction conditions.

$$MgCl_2 + 2M \longrightarrow Mg + 2MCl \qquad (4.4)$$

$$M = Li, Na, K$$

In Grignard reactions, iodine is used as a reaction initiator, and other Grignard reagents, 1,2-bromoethane and methyl iodide are also used as the initiator [4,15,21]. Diethyl ether is used as an ordinary solvent. Tetrahydrofuran, for which the electron donor ability is higher than in ethyl ether, is suitable for low reactive aryl halides, vinyl halides and chlorides. In contrast, diethyl ether, for which the electron donor ability is low, suppresses the coupling reaction of the organic group. Hence diethyl ether is preferable for the reaction of reactive alkyl iodides or allyl halides [15].

The solubility of hydrocarbons such as benzene, toluene, and C_5–C_{12} alkanes are low for Grignard reagents. Thus they are not used as a single solvent but mixed solvents with diethyl ether or THF are used. Isopropyl ether, dioxane, triethylamine and HMPA (hexamethylphosphoric triamide) are also used as the solvent [15].

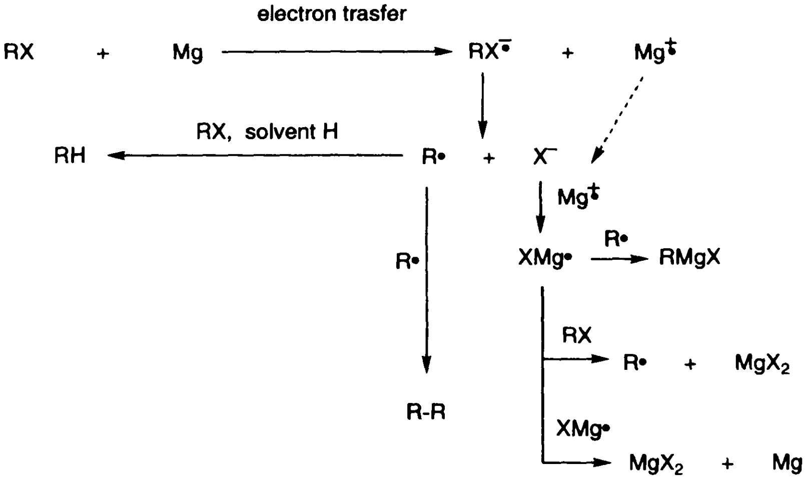
A Grignard reagent is not simply RMgX in ether and they are considered to form Schlenk equilibrium as shown in eq. (4.5) [15]. It is presumed that the formation reaction of Grignard reagents proceeds as shown in Scheme 4.1 [22,23].

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \rightleftharpoons R_2Mg{\bullet}MgX_2 \qquad (4\text{-}5)$$

An electron transfers from magnesium metal to the organic halide and the organic halide becomes an anion radical. Subsequently, the anion radicals separate into organic radicals and halogen anions. Magnesium becomes a radical cation by the electron transfer, and it bonds with a halogen anion to give XMg·. Furthermore, it couples with the organic radical R· to form RMgX by radical coupling.

The direct proof that the Grignard formation reaction proceeds in this way was given by CIDNP (Chemical Induced Dynamic Nuclear Polarization) in 1972 by Bodewitz *et al.* [22,23]. They found the variation of peaks caused by the formation of the radical using CIDNP by measurement of the methylene proton in the Grignard formation reaction of CH_3CH_2I or $(CH_3)_2CH_2CH_2Br$.

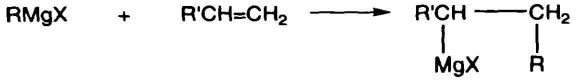
Grignard reagents are prepared mainly by the reaction shown in eq. (4.3). The others are prepared by the reactions shown in eqs. (4.6)–(4.8). The reactions shown in eq. (4.6) are reactions with compounds having an active hydrogen. For example, the reactions with acetylenes, cyclopentadiene, indene, fluorene.



Scheme 4.1 [22,23]

$$RMgX + R'H \longrightarrow R'MgX + RH \quad (4.6)$$

$$RMgX + R'X' \longrightarrow R'MgX + RX' \quad (4.7)$$



$$RMgX + R'CH{=}CH_2 \longrightarrow \underset{MgX}{R'CH}-\underset{R}{CH_2} \quad (4.8)$$

The reaction with acetylene shown in eq. (4.9) shows the higher reactivity when the basicity of the solvent is low.

$$EtMgBr + BuC{\equiv}CH \longrightarrow BuC{\equiv}CMgBr + C_2H_6 \quad (4.9)$$

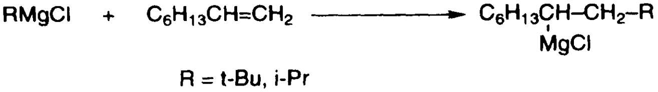
The order of the reactivity regarding the alkyl groups of the solvent is as follows [24].

$$i\text{-}Pr_2O > Bu_2O > Et_2O > THF > 2\text{-}MeTHF$$

Metal–halogen exchange reactions as shown in eq. (4.7) are a standard synthetic reaction for organolithium compounds. However the literature for organomagnesium compounds is relatively few [15]. For example, Grignard reagents having an electron withdrawing group such as polyhalides as shown in eq. (4.10), are obtained in high yields [25].

$$\mathrm{EtMgBr} + \mathrm{C_6F_5Br} \xrightarrow[\text{in THF}]{\text{room temp}} \underset{98\ \%}{\mathrm{C_6F_5MgBr}} + \mathrm{EtBr} \qquad (4.10)$$

The reactivity of addition reactions of straight-chain alkyl and aryl Grignard reagents to alkenes is not high, but the secondary or tertiary derivatives are reactive, and bulky organic group selectively bonds to the terminal carbon [26].



$$\mathrm{RMgCl} + \mathrm{C_6H_{13}CH{=}CH_2} \longrightarrow \mathrm{C_6H_{13}\underset{MgCl}{C}H{-}CH_2{-}R} \qquad (4.11)$$

$$\mathrm{R = t\text{-}Bu,\ i\text{-}Pr}$$

Grignard reagents are also synthesized by addition reactions of alkynes, addition reactions of unsaturated compounds having C=S groups, reactions of cycloalkanes, reactions with organolithium compounds or organomercury compounds, etc. [4,15,27,28].

4.3.2 R_2Mg

R_2Mg as shown in eq. (4.5) (Schlenk equilibrium) is one component in the equilibrium state of a Grignard reagent (RMgX). So R_2Mg is able to be isolated by shifting the equilibrium of the Grignard reagents. For example, as shown in eq. (4.12), 1,4-dioxane is added to the ether solution of a Grignard reagent, and MgX_2 forms a complex with dioxane. The complex precipitates since it is slightly soluble, and R_2Mg is obtained from the solution [27,29–31].

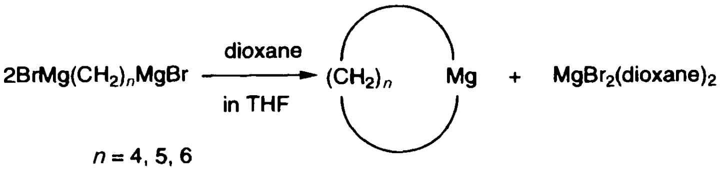
For example, when dioxane in limited amounts is added to a diethyl ether solution of neopentylmagnesium chloride, the complex of $MgCl_2$ with dioxane precipitates, and this complex is separated by centrifugation. Ether and dioxane from the supernatant solution is removed under reduced pressure, and then the colorless prismatic crystal of $(CH_2\text{-}t\text{-}Bu)_2Mg$ yields at 90–110 °C/10^{-2} mmHg by sublimation (eq. (4.13)) [29].

$$\underset{0.43\ \mathrm{mol}}{t\text{-}\mathrm{Bu\text{-}CH_2MgCl}} \xrightarrow[\text{in ether 500 ml}]{\text{dioxane 44 ml}} \mathrm{MgCl{\bullet}(dioxane)_2} + \underset{\text{colorless prism}}{\mathrm{Mg(CH_2\text{-}}t\mathrm{\text{-}Bu)_2}} \qquad (4.13)$$

In the preparation of Grignard reagents, as MgX_2 has a low solubility in a hydrocarbon solvent, MgX_2 precipitates in the ether solution containing a large amount of hydrocarbon as shown in eq. (4.14). R_2Mg forms [32].

$$\underset{0.43\ \text{mol}}{2\,sec\text{-BuCl}} + 2\text{Mg} \xrightarrow[\substack{\text{in Me}_2\text{O and hexane} \\ \text{Me}_2\text{O } 10\ \%}]{\text{room temp}} \underset{80\ \%}{sec\text{-Bu}_2\text{Mg}} + \text{MgCl}_2 \downarrow \quad (4.14)$$

When the reaction shown in eq. (4.12) is applied to bis Grignard reagents, as shown in eq. (4.15), cyclic magnesiacycloalkane forms [33,34].



$$\underset{n = 4,\,5,\,6}{2\text{BrMg(CH}_2)_n\text{MgBr}} \xrightarrow[\text{in THF}]{\text{dioxane}} \overbrace{(\text{CH}_2)_n \quad \text{Mg}} + \text{MgBr}_2(\text{dioxane})_2 \quad (4.15)$$

Grignard reagents react with organolithium compounds and LiX precipitates since the solubility of LiX is low and R_2Mg forms as shown in eq. (4.16) [35]. Even if the organolithium compounds react with magnesium dichloride in place of the Grignard reagents, R_2Mg also forms as shown in eq. (4.17) [35].

$$\text{RLi} + \text{RMgX} \xrightarrow[\text{in ether}]{} \text{R}_2\text{Mg} + \text{LiCl} \downarrow \quad (4.16)$$

$$2\text{RLi} + \text{MgCl}_2 \xrightarrow[\text{in benzene or hexane}]{} \text{R}_2\text{Mg} + 2\text{LiCl} \downarrow \quad (4.17)$$

R_2Mg is also prepared by the transmetalation of organomercury compounds as shown in eq. (4.18) [36]. As described above, the preparation method of R_2Mg by formation of a MgX_2 complex with dioxane and by precipitation of MgX_2 in a slightly soluble hydrocarbon solvent, tends to retain a trace of halogen. However, the transmetalation is available for preparation of a high purity R_2Mg as shown in eq. (4.18).

$$\text{Et}_2\text{Hg} + \text{Mg} \xrightarrow{\text{HgCl}_2,\ 130\ ^\circ\text{C}} \text{Et}_2\text{Mg} + \text{Hg-Mg} \quad (4.18)$$

4.4 STRUCTURES OF ORGANOMAGNESIUM COMPOUNDS

Magnesium tends to associate. Magnesium forms various kinds of coordination structures, and furthermore forms an electron deficient bond. Therefore, these characteristics make the clarification of the structure of Grignard reagents difficult. However, recently many complicated structures have been clarified step by step by utilization of radioisotopes and by X-ray diffraction studies [37].

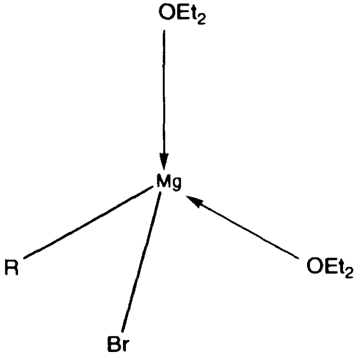
$MgBr_2$ containing the radioisotope Mg^{28}, is added to MeMgBr, and immediately $Mg^{28}Br_2$, $MeMg^{28}Br$ and Me_2Mg^{28} form. On the other hand, the methyl proton of MeMgBr in the ether solution shows one kind of peak. However, cooled to −100 °C, the peak splits into two peaks of MeMgBr and Me_2Mg. From these data, it is considered that the Schlenk equilibrium of MeMgBr is very fast at room temperature [38].

One mole of ether is added to one mole of PrMgI to generate 6.63 kcal, two mole of ether is added to the same mole of PrMgI to generate 12.30 kcal. However, even if more ether is added to the same solution, the generation of heat does not increase. Therefore, in PrMgI, it is considered that the state coordinated with two mole of ether is the most stable thermodynamic state [39].

In 1964, the structures of PhMgBr and EtMgBr are found by X-ray diffraction studies to have a four-coordination, tetrahedral structure coordinated with oxygens of two ethers as shown in Figure 4.1 [40–42]. The ether adducts are obtained by placing the ethyl ether solution of Grignard reagents in an L-shaped vessel and by cooling with liquefied nitrogen to crystallize the adduct [40].

These adducts are able to be expressed as $RMgX{\cdot}L_2$. The ligand L is not only ether, but also THF, dioxane, TMEDA ($Me_2N{-}CH_2CH_2{-}NMe_2$), etc. It has been found that all of these adducts also form four-coordination, tetrahedral structures similar to the structure shown in Figure 4.1 [37].

The bond angles (L−Mg−L) of the solvent molecule become small by Bent's rule (in the sp^n hybridization orbitals, *n* is the smaller, the contribution of s-orbitals is the larger, the electronegativity of the orbitals is the higher by lifting more s-electrons to the p-orbitals. If the electronegativity of the ligand is the larger, and if the electronegativity of the orbital which bond with the ligand is the smaller, the



	R = Et	R = Ph
O−Mg−O	101.2 °	
Br−Mg−O	103.0 °, 103.7 °	103.3 °, 109.8 °
C−Mg−Br	125.0 °	

Figure 4.1 Molecular configuration of $RMgBr{\cdot}2Et_2O$ [40–42].

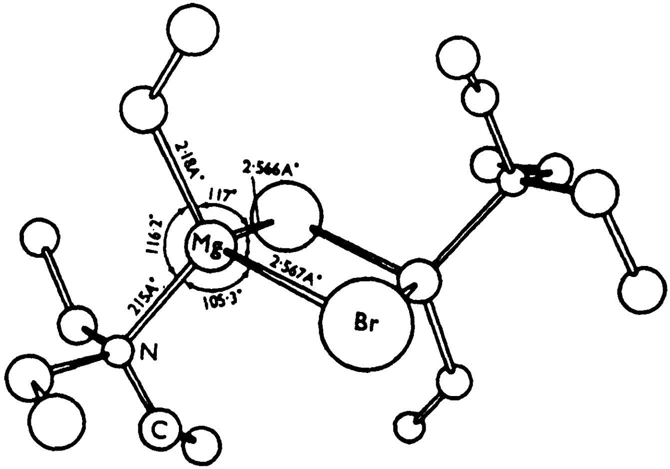


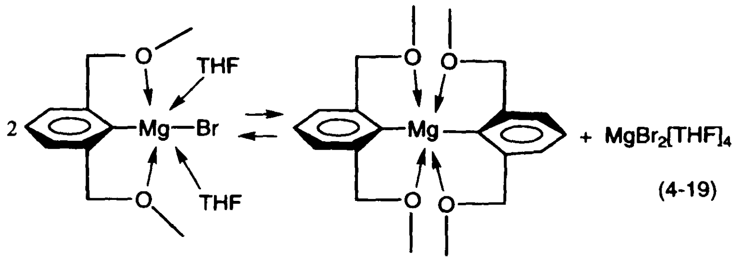
Figure 4.2 Molecular structure of $[EtMgBr{\cdot}NEt_3]_2$ [43].

stability is the higher, and the contribution of p-orbitals is larger) [37]. For example, as shown in Figure 4.1, C–Mg–Br is 125.0°. However, L–Mg–L of $EtMgBr{\cdot}(OEt_2)_2$ become smaller (101.2°) [42].

Grignard reagents tend to take a monomeric structure in THF since the coordination of THF is stronger than that of diethyl ether. But, in weak coordination solvents such as triethylamine and diisopropyl ether, the Grignard reagents form a dimer having a halo-bridged structure as shown in Figure 4.2 [43]. The order of the ability of bridge formation is as follows [37].

alkoxides, amide > halogens > alkyl, amyl

In the Grignard reagent of a 2,6-substituted aryl compound, as shown in eq. (4.19), most of the THF is removed from the reaction solution by distilling, and *n*-hexane is added and cooled to yield the R_2Mg type compound (the right-hand compound of the reaction as shown in eq. (4.19)) in the Schlenk equilibrium as crystals. The structure of R_2Mg is found such that magnesium is intramolecularly



(4-19)

Pseudo-octahedral structure

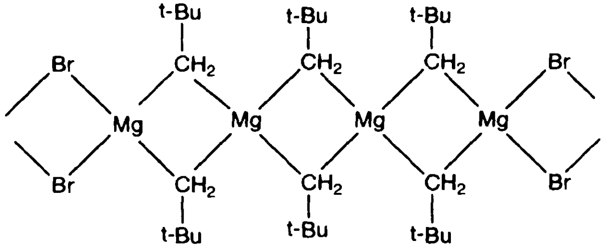


Figure 4.3 Polymeric crystal structure of $[(Np_2Mg)_2{\cdot}(NpMgBr)_2]_n$ [45].

coordinated by four oxygen atoms of methoxymethyl groups and R_2Mg has a six-coordination distorted octahedral structure [44].

Dioxane is added to the synthetic reaction solution of Grignard reagents as shown in eq. (4.12) to precipitate MgX_2, and then R_2Mg is isolated. However, in the case of neopentylmagnesium bromide which has a branched organic group, the separation between R_2Mg and $MgBr_2$ is difficult. The crystal which is obtained from the solution on removal of the complex of $MgBr_2$ and dioxane, $MgBr_2$ still remains. This crystal is found to be a polymeric compound $[(Np_2Mg)_2{\cdot}(NpMgBr)_2]_n$ having two kinds of bridged structure with halogen and neopentyl groups as shown in Figure 4.3 [45].

Ph_2Mg is dissolved in THF/*n*-hexane (1 : 1) solution, and cooled to precipitate the crystal of $Ph_2Mg(THF)_2$. $Ph_2Mg(THF)_2$ has a tetrahedral structure as shown in Figure 4.1 [44]. But if a THF solution of Ph_2Mg is diluted with a large quantity of benzene and is allowed to stand for several months, then THF coordinated to Mg is liberated gradually to yield polymeric $[Ph_2Mg]_n$. $[Ph_2Mg]_n$ is found to be a polymer having a bridged structure with the carbon of benzene by X-ray diffraction studies. $[Ph_2Mg]$ is a living polymer and the phenyl carbon forms electron deficient bonds, i.e., three-center two-electron bonds and the magnesium atom has a tetrahedral structure [46].

On heating magnesium at 500–600 °C, and passing cyclopentadiene over it gives Cp_2Mg as white crystals [47]. Cp_2Mg is found to be a sandwich structure, similar to ferrocene, by gas phase electron diffraction [48].

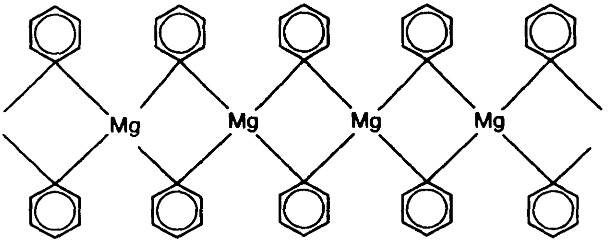


Figure 4.4 Crystal structure of polymeric diorganomagnesium [46].

Organomagnesium compounds are found to form four coordinated tetrahedral structures as shown in Figures 4.1–4.4, the others having a six-coordinated octahedral structure as shown in eq. (4.19). Further, the compounds from two coordinated compounds to eight coordinated compounds are found as shown in Figure 4.5 [37]. Since the ability of association of magnesium is high, magnesium tends to form a bridge structure with halogen, oxygen, nitrogen and carbon atoms, to form the adduct with solvent and to form various kinds of coordination structures. Also Schlenk equilibrium varies with temperatures, solvents and concentrations, and Schlenk equilibrium changes rapidly at room temperature. These cause many difficulties to clarifying the structure of the Grignard reagents. But it becomes unambiguous that they have mainly tetrahedral structures as shown in Figures 4.1–4.4.

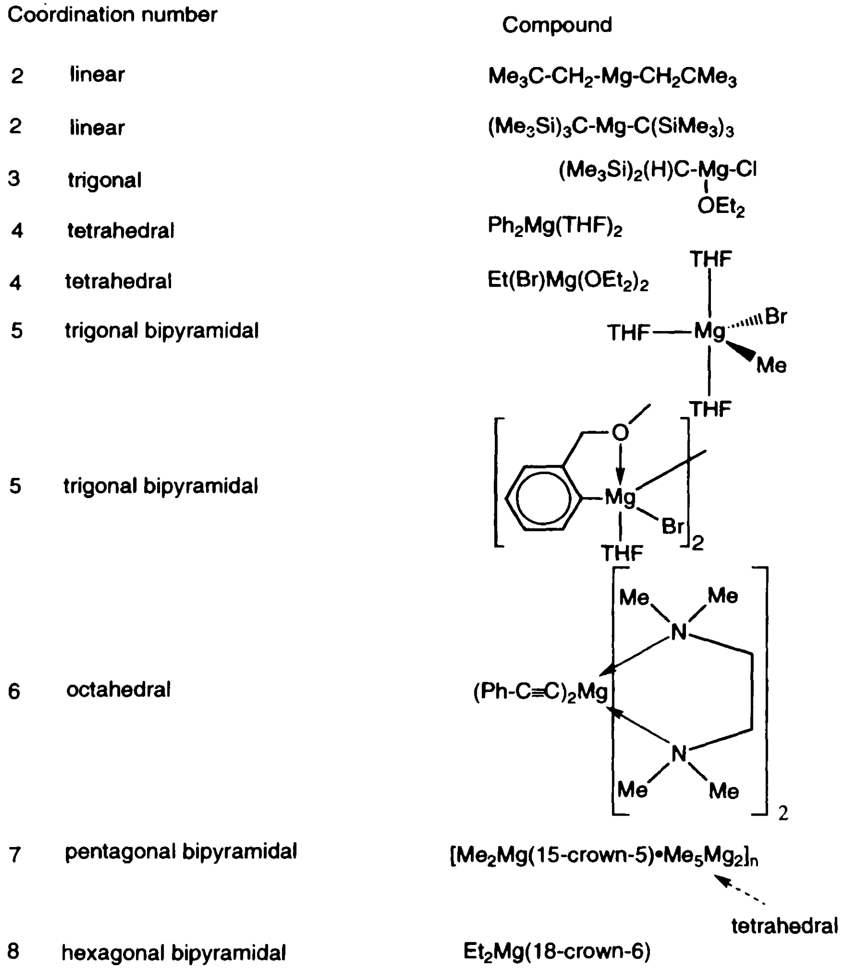


Figure 4.5 Structure of organomagnesium compounds [37].

Recently, as components of Schlenk equilibrium, the structures of $RMgX$, MgX_2 and $(Me_3Si)_3CMg(\mu\text{-}Br)_3Mg(THF)_3$, $EtMgCl\cdot MgCl_2(THF)_3$ bonded with solvent molecules, are determined by X-ray diffraction studies [48a,48b].

4.5 PROPERTIES OF ORGANOMAGNESIUM COMPOUNDS

Organomagnesium compounds are generally colorless solids, nonvolatile, soluble in hydrocarbons, thermally stable up to 100–170 °C, but at higher temperatures they can decompose explosively.

Organomagnesium compounds are sensitive to oxygen and moisture in air. However, in ethereal solution, the relatively heavy ether vapor protects them to some extent from exposure to air. For a small amount or a very pure preparation, an inert atmosphere of nitrogen or preferably argon is recommended.

Many kinds of structures of organomagnesium compounds are shown in the previous section. One cause of the difference of these structures is the different shift of Schlenk equilibrium caused by the difference in the organic group. The Schlenk equilibrium also varies according to the differences of halogens, solvents, concentrations and temperatures. In diethyl ether, the major component is RMgX, whereas in THF an almost statistical distribution exists, i.e., $R_2Mg : MgX_2 : 2RMgX = 1 : 1 : 2$ [13].

The reactivities of organic halide to magnesium metal are in the order of;

$$RI > RBr > RCl$$

However, in contrast with this, the order of yields is generally as follows:

$$RCl > RBr > RI$$

The RI is very reactive and side reactions occur frequently, thus the yield is low. RBr is most suitable for the production of Grignard reagents, but is frequently replaced in industrial applications by the cheaper chloride.

Organomagnesium compounds are soluble in ethers, dioxane and pyridine, etc., and form the adducts. In the case of of an ether adduct, when it is heated at room temperature or higher, it forms a white polymeric solid with liberation of the ether.

Organomagnesium compounds easily react with compounds having an active hydrogen such as water, alcohols, amines and acetylenes, halides and carbonyl compounds.

$$RMgX \quad + \quad HC{\equiv}C\text{–}n\text{-}Bu \longrightarrow RH \quad + \quad XMgC{\equiv}C\text{–}n\text{-}Bu \qquad (4.20)$$

The reactivity of alkyl Grignard reagents with acetylene compounds as shown in eq. (4.20), is in the following order regarding the alkyl groups under consideration from the amounts of the hydrocarbon gas generated in the reaction

$$i\text{-Pr} > \text{Et} > n\text{-Pr} > \text{Me}$$

[49]. The results show that the more the numbers of β-hydrogen, the higher is the reactivity. Hence, it is considered that the reactivity of the alkyl anion having the group which tends to form the hyperconjugation with methyl is high [27].

With the Grignard reagents different from organolithium compounds, the reactivities of halogen–metal exchange reactions and additions to carbon–carbon double bonds are low. And with Grignard reagents, 1,4-additions to α,β-unsaturated ketones tend to proceed since the nucleophilicity of Grignard reagents is low, which is also different from organolithium compounds.

4.6 APPLICATIONS OF ORGANOMAGNESIUM COMPOUNDS

There are various other kinds of organomagnesium compound besides Grignard reagents (RMgX). Grignard reagents are used for various organic syntheses because of their easy handling and the reactivities described above.

As Grignard reagents occasionally cause a very violent exothermic reaction, we simply think that it may be too difficult to use for industrial purposes. However, by the accumulation of technical knowledge such as the control of the addition rate of raw materials; the prevention of peroxide generation by thorough dehydration and degasification; the prevention of ignition and explosion by the countermeasures of heat removal and of removal of static electricity caused by dry solvent, Grignard reactions are industrially used in the production of the following four compounds [3–5].

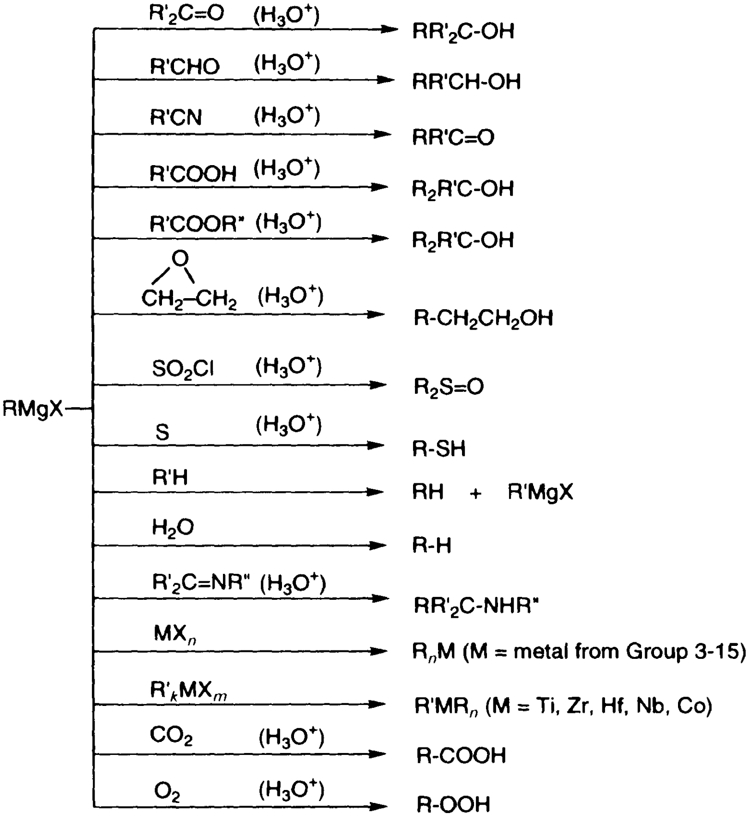
(1) intermediates of pharmaceuticals and agrochemicals
(2) perfumes and their related compounds
(3) chemicals and phosphines
(4) organometallic compounds and others

4.6.1 SYNTHETIC REACTION WITH GRIGNARD REAGENTS

The representative synthetic reactions with Grignard reagents are shown in Scheme 4.2 [4,13,28,35,50,51]. The most important of these reactions are the syntheses of secondary or tertiary alcohols by addition reaction to carbonyl groups of aldehydes and ketones. Acid chlorides, acid anhydrides, esters and nitriles react with excess Grignard reagents to give ketones at first. Subsequently, the Grignard reagents react with the ketones to give tertiary alcohol. The reactivity of the Grignard reagents is as follows [51]:

acid chlorides > aldehydes > ketones > acid anhydrides > esters > nitriles

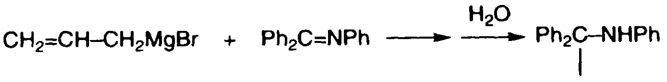
As the reactivities of nitriles are lower than those of the other carbonyl compounds, they are used for the synthesis of ketones which are the intermediates of Grignard reactions, especially when nitriles are used as the raw materials of the syntheses of asymmetric ketones [51].



Scheme 4.2 [4,13,28,38,50,51]

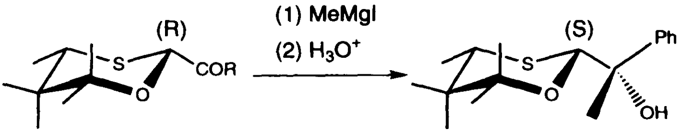
Formaldehyde, as an aldehyde, gives the primary alcohol in which the carbon number is increased by one. Ethylene oxide gives the primary alcohol in which the carbon numbering increased by two. Carbon dioxide is used for the preparation of the carboxylic acid in which the carbon number is increased by one [51].

Grignard reagents react with imines to give the corresponding amines. However, the reactivity of the carbon–nitrogen double bond is lower than that of the carbon–oxygen double bond. Further, imines easily give metaloenamines $(-\text{C}{=}\text{C}-\overset{|}{\text{N}}-\text{MgX})$ by a hydrogen extraction reaction at the α-position. Hence, with imines not having a hydrogen at the α-position or in using reactive allyl or benzyl Grignard reagents, imines give their adducts in high yields. For example, allyl Grignard reagents react with N-diphenylmethyleneaniline to give the allyl adduct in 95 % yield as shown in eq. (4.21) [52].



$$CH_2{=}CH{-}CH_2MgBr \ + \ Ph_2C{=}NPh \longrightarrow \xrightarrow{H_2O} \underset{\displaystyle CH_2{-}CH{=}CH_2}{\underset{|}{Ph_2C}}{-}NHPh \qquad (4.21)$$

Grignard reagents, as described above, tend to be coordinated by a hetero atom such as oxygen or nitrogen, and to have various kinds of coordination structure forms as shown in Figure 4.5. For example, if there is a hetero atom near the carbonyl group as shown in eq. (4.22), magnesium is able to be coordinated by both the oxygen of the carbonyl group and the other hetero atom. Asymmetric synthesis is able to proceed since the reaction proceeds on fixing the attacking direction of Grignard reagents by these coordinations [53].

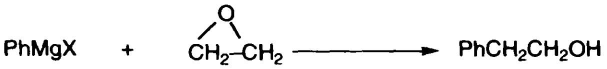


(4.22)

95 %, $[\alpha]^{25}_D$ −40.9 ° ($CHCl_3$)

Industrial applications of Grignard reagents are shown in eqs. (4.23)–(4.27). The reactions shown in eqs. (4.23) and (4.24) are preparation methods for phenylalkylalcohols which are the raw materials for soaps and detergents, etc. The reaction shown in eq. (4.25) is the preparation method for a pharmaceutical Methentermine. The reaction shown in eq. (4.26) is the preparation method for an agrochemical Dimite, and the reaction shown in eq. (4.27) is the preparation method for *p*-chlorostyrene which is used as a monomer of functional polymers and a curing accelerator for unsaturated polyesters, polyurethanes, etc. [3–5].

$$PhCH_2MgX + Me_2C{=}O \longrightarrow PhCH_2C(Me_2)OH \quad (4.23)$$

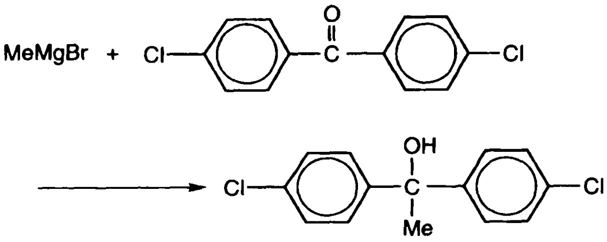


$$PhMgX + \overset{O}{CH_2{-}CH_2} \longrightarrow PhCH_2CH_2OH$$

(4.24)

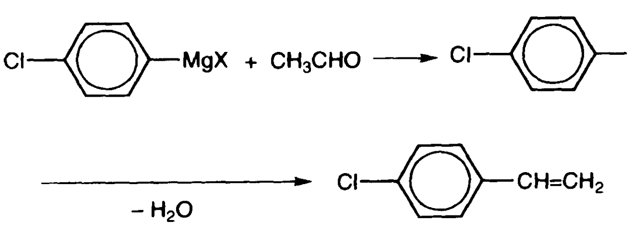
$$PhCH_2MgX + Me_2C{=}NMe \longrightarrow PhCH_2C(Me_2)NHMe \quad (4.25)$$

Methentermine



(4.26)

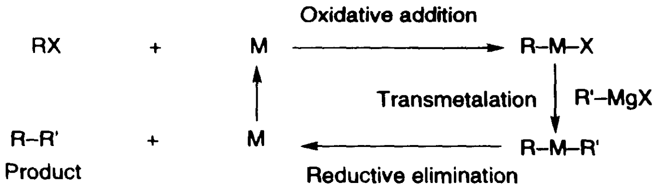
Dimite



(4.27)

4.6.2 TRANSITION-METAL CATALYZED SYNTHETIC REACTIONS WITH GRIGNARD REAGENTS

Grignard reagents are not available for substitution reaction of ethers, thioether and phosphoric esters, and addition reactions to unsaturated compounds since the reactivities of Grignard reagents are low. In the presence of transition metal compounds, the oxidative addition and reductive elimination as the representative reactions of the transition-metal catalysts proceeds. The reaction with halides is shown in Scheme 4.3 [54]. Grignard reagents give the organic group to the transition metal by transmetalation after oxidative addition. The organotransition metal compounds (R–M–R′) are very liable, immediately decompose (reductive elimination) to yield the desired coupling products and the transition catalysts are regenerated.



Scheme 4.3 [54]

The many coupling reactions of transition-metal catalyzed Grignard reactions with organic halides have been studied frequently. However, their synthetic usefulness is not found since there are many side reactions. But the wide variety of researches started mainly from the early 1970s [54–56]. In particular, Kumada *et al.* [57–96] have energetically studied centering around nickel–phosphine complexes (NiL_2Cl_2), and also palladium catalysts from 1972 and they have found many catalysts having high stereoselectivities.

These transition elements are Fe, Co, Ni, Pd, Cu and Ag. These metal catalysts have respective characteristics. For example, the representative catalytic actions are as follows: silver is for alkyl–alkyl homo-coupling, copper is for cross-coupling, nickel and iron are for cross-coupling containing unsaturated halides such alkenyl and aryl halides [56]. These basic reaction examples are shown in eqs. (4.28)–(4.32) [55,56]. Kumada *et al.* synthesized many compounds as ligands which have

$$n\text{-BuMgBr} + n\text{-BuBr} \xrightarrow{[\text{Ag}],\ 25\ ^\circ\text{C},\ 5\ \text{hr}} \underset{79\ \%}{n\text{-Bu-}n\text{-Bu}} \qquad (4.28)$$

$$2t\text{-BuMgBr} + \text{TsO(CH}_2)_{12}\text{OTs} \xrightarrow[\substack{\text{THF / Et}_2\text{O} \\ -78\ ^\circ\text{C} - \text{room temp}}]{\text{Li}_2\text{CuCl}_4\ (0.2\ \%)} \underset{99\ \%}{t\text{-Bu-(CH}_2)_{12}\text{-}t\text{-Bu}} \qquad (4.29)$$

$$\text{BrMg(CH}_2)_6\text{MgBr} + 2\text{Br(CH}_2)_6\text{Br} \xrightarrow[\text{THF}]{\text{Li}_2\text{CuCl}_4\ (1\ \%)} \underset{70 - 80\ \%}{\text{Br(CH}_2)_{18}\text{Br}} \qquad (4.30)$$

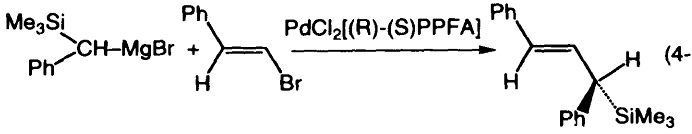
$$i\text{-PrMgBr} + \text{BrCH=CH-CH}_3 \xrightarrow[\text{THF}]{\text{Fe (I)}} \underset{60\ \%}{i\text{-Pr-CH=CH-CH}_3} \qquad (4.31)$$

$$\text{PhCl} + \text{RMgX} \xrightarrow{[\text{Ni(dppp)Cl}_2]} \underset{>95\ \%}{\text{Ph-R}} \qquad (4.32)$$

R = Me, Et, Pr, C_6H_{11}

dppp = $Ph_2P(CH_2)_3PPh_2$

an asymmetric carbon or are stereoasymmetric [84,85,88] and they prepared many asymmetric compounds. For example, as shown in eq. (4.33), the optically active compounds are prepared with the ferrocenylphosphine ligand having an asymmetric carbon [88,93].

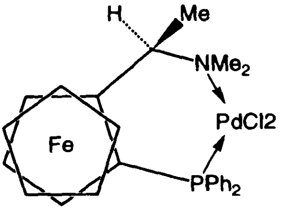


(4-33)

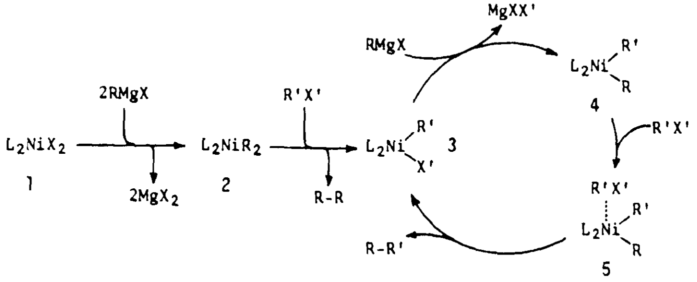
93 % yield, 95ee(R)

(R)-(S)PPFA = (R)-N,N-Dimethyl-1-[(S)-2-(diphenylphosphino)-ferrocenyl]ethylamine

PdCl2[(R)-(S)-PPFA]



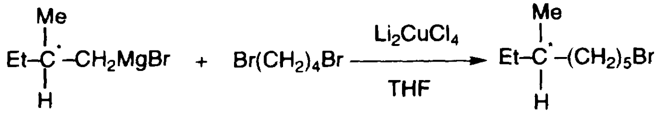
In the transition-metal catalyzed asymmetric Grignard coupling, Kumada *et al.* proposed a reaction mechanism, as shown in Scheme 4.4 [78], in which the active site is the organotransition metal compounds (R—M—R′) which can be obtained by the reaction of organotransition metal compounds with the Grignard reagent [78].



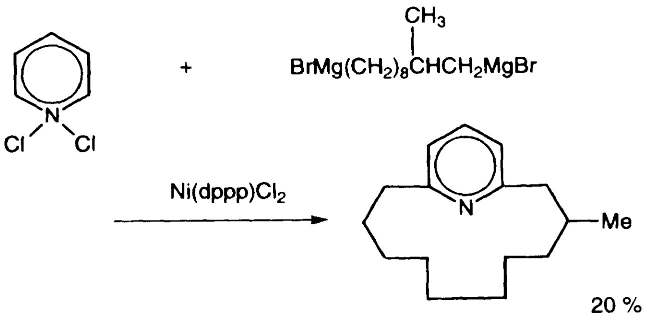
Scheme 4.4 Mechanism of the nickel–phosphine catalyzed asymmetric Grignard cross-coupling [78]

If the organic halides react directly with organotransition metal compounds since the organotransition metal compounds are very reactive as shown in Scheme 4.3, and the reaction product R–M–X is the active site. However, as the reactivity of organic halides is lower than that of Grignard reagents, Grignard reagents react with the transition metal compounds to give the active site of the active intermediates (R–M–R). Then the intermediates react with organic halides to reproduce the oxidative addition product (R–M–X). Then the reaction proceeds continuously as shown in Scheme 4.4 [66].

These Grignard reactions with transition metal compounds are used for many reactions [54–56]. For example, preparation of a synthetic intermediate of sex hormones [56,97] and muscopyridine of the odoriferous constituents of natural musk from the musk deer [98], are shown in eqs. (4.34) and (4.35).



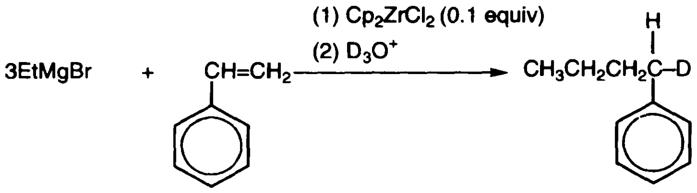
$$\mathrm{Et{-}\underset{H}{\overset{Me}{C^{*}}}{-}CH_2MgBr} + \mathrm{Br(CH_2)_4Br} \xrightarrow[\mathrm{THF}]{\mathrm{Li_2CuCl_4}} \mathrm{Et{-}\underset{H}{\overset{Me}{C^{*}}}{-}(CH_2)_5Br} \quad (4.34)$$



(4.35)

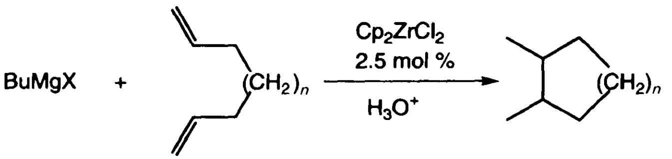
Muscopyridine

In the addition reaction of Grignard reagents to a carbon–carbon unsaturated bond, the yields and selectivities become higher by using transition metal catalysts, and so these reactions came to public notice. Metal compounds of Ti, Ni, Cu and Zr are used for the catalysts [55,56,99]. For example, the adduct is obtained in a high yield by a carbometalation reaction with zirconium catalysts as shown in eq. (4.36) [100]. On the other hand, cyclization proceeds in a high yield by using a diene as shown in eq. (4.37) [101].



(4.36)

95 % yield, >99 %D



(4.37)

$n = 1, 2$ 90 - 100 %

4.6.3 SYNTHESES OF ORGANOMETALLIC COMPOUNDS AND OTHERS

Grignard reagents are most used for industrial preparation of organometallic compounds [3]. Previously, when a large amount of tetraethyllead was used as gasoline octane improvers, the tetraethyllead was prepared with Grignard reagents as shown in eq. (4.38).

$$12EtMgX + 6PbX_2 \xrightarrow{\qquad} \underset{60-80\ \%}{3Et_4Pb} + Pb + 12MgX_2 \quad (4.38)$$

Organomercury compounds were produced by the reaction shown in eq. (4.39) and they were used for agrochemicals such as disinfectants of seeds. But, their poisonous character was pointed out earlier than that of organolead compounds. In Japan, the use of agricultural mercurials was prohibited in 1968. After that, agricultural organomercury compounds have not been prepared [3].

$$RMgX + HgCl_2 \xrightarrow{\qquad} RHgX \quad (4.39)$$

As described in Chapter 10 on organotin compounds [3], they are used for PVC stabilizers, polymerization catalysts for polyurethanes, silicon, etc., wood preservatives and agrochemicals. Organotin compounds are prepared by many preparation methods. The Grignard method as shown in eq. (4.40) is very useful for the preparation of long chain alkyltin compounds, especially tetraoctyltin and tetrabutyltin. $(Oct)_2SnCl_2$ prepared from tetraoctyltin is perfectly nonpoisonous, and is used as PVC additives in large amounts for food packing [3.6].

$$4RMgX + SnCl_4 \longrightarrow R_4Sn + 4MgCl_2 \qquad (4.40)$$

$$R = Bu, Oct$$

Oganogermanium componds (Chapter 9), organotitanium compounds (Chapter 12) and organocopper compounds (Chapter 22) are prepared by the reaction as shown in eqs. (4.41)–(4.43).

$$4MeMgI + GeCl_4 \longrightarrow \underset{93\ \%}{Me_4Ge} \qquad (4.41)$$

$$2CpMgX + TiCl_4 \longrightarrow Cp_2TiCl_2 \qquad (4.42)$$

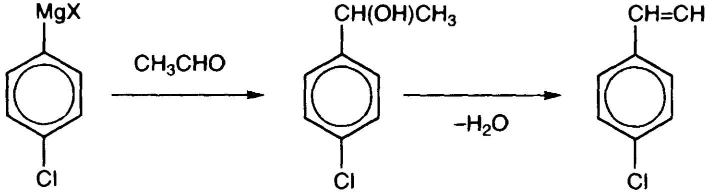
$$RMgX + CuX \longrightarrow RCu + MX_2 \qquad (4.43)$$

As the other industrial uses of Grignard reagents, there are preparations of phosphines and *p*-chlorostyrene. The phosphines are used for the preparation of vitamin as the reagents for the Wittig reaction, curing materials for epoxy resins, stabilizers for various kinds of synthetic resins, lubricant additives, etc. and they are prepared by the reaction shown in eq. (4.44) [3].

$$3RMgX + PCl_3 \longrightarrow R_3P \qquad (4.44$$

$$R = n\text{-Bu, cyclohexyl, Ph}$$

p-Chlorostyrene is used for a monomer for functional polymers and curing accelerators for unsaturated polyesters, polyurethanes, etc., and it is synthesized by various methods. Of these, one reaction with a Grignard reagent is shown in eq. (4.45).



(4.45)

At the end of this chapter I am very grateful to Emeritus Professor Makoto Kumada of Kyoto University for providing me with a many articles, reviews, books and brochures.

REFERENCES

[1] M. Kumada, *Kagaki*, **44** (1989) 34.
[2] P.R. Jones and E. Southwick, *J. Chem. Educ.*, **47** (1970) 290.
[3] Y. Jitsu and M. Umeno, *Finechemicals*, **10**/1(1984)15.
[4] M. Umeno and M. Hamada, *Yuki Gosei Kagaku Kyokaishi*, **38** (1980) 1196.
[5] M. Umeno and F. Abe, *Finechemicals*, **15**(11)(1986)11.
[6] I. Omae, *Organotin Chemistry, J. Organomet. Chem. Library 21*, Elsevier, Amsterdam, 1989.
[7] *Kagaku Binran Kisoshen I*, Japan Chemical Society ed., Maruzen, Tokyo, 1984.
H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York (1979).
[8] *Kagaku Daijiten*, Tokyo Kagaku Dojin, p. 385, 1989.
[8a] *1987 Statistical Yearbook*, Thirty-sixth issue, Department of International Economic and Social Affairs, Statistical Office, United Nations, New York, 1990.
[8b] T. Imai, *Kagaku Keizai*, April(1994)55.
Sekai Kokusei Zukai 1998/1996, Kokuseisha, Tokyo, 1996.
[9] *Kagaku Binran Ooyohen*, Japan Chemical Society ed., Maruzen, Tokyo, p. 287, 1980.
[10] *11691 no Kagaku Shohin*, Kagaku Kogyo Nipposha, p. 147, 1991.
[11] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed. John Wiley, New York, vol. 14, p.570, 1980
[12] *Rikagaku Jiten*, Iwanami Shoten, p. 1250, 1987.
[12a] *Nikkei Sangyo Shinbun*, April 2, 1992.
[13] *Ullmann's Encyclopedia of Industrial Chemistry*, vol. A15, Fifth ed., VCH, Weinheim, p. 559, 1990.
[13a] Kirk-Othmer, *Encyclopedia of Chemical Technology*, Fourth ed., vol. 5, p.622, John Wiley, New York, 1995.
[14] *Kagaku Daijiten*, Tokyo Kagaku Dojin, p. 2272, 1989.
[15] W.E. Lindsell, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel eds., Pergamon Press, Oxford, vol. 1, p. 155, 1982
[16] *Methoden der Organishen Chemie*, Houben-Weyl, Band XIII/2a, p. 47, 1973.
[17] R.D. Rieke and S.E. Bales, *J. Am. Chem. Soc.*, **96** (1974) 1775.
[18] R.D. Rieke, *Acc. Chem. Res.*, **10** (1977) 301.
[19] K.J. Klabunde, H.F. Efner, L. Satek and W. Donley, *J. Organomet. Chem.*, **71** (1974) 309.
[20] R.D. Rieke, S.E. Bales, P.M. Hudnall, T.P. Burns and G.S. Poindexter, *Org. Syn. Coll.*, **6** (1988) 845.
[21] *Yuki Kinzoku Kagobutsu, Gosei oyobi Riyoo*, A. Yamamoto ed., Tokyo Kagaku Dojin, p. 40, 1991.
[22] H.W.H.J. Bodewitz, C. Blomberg and F. Bickelhaupt, *Tetrahedron*, **29** (1973) 719.
[23] H.W.H.J. Bodewitz, C. Blomberg and F. Bickelhaupt, *Tetrahedron Lett.*, (1972) 281.
[24] J.H. Wotiz and G.L. Proffitt, *J. Org. Chem.*, **30** (1965) 1240.
[25] W.L. Respess and C. Tamborski, *J. Organomet. Chem.*, **11** (1968) 619.
[26] H. Lehmkuhl, O. Olbrysch, D. Reinehr, G. Schomburg and D. Henneberg, *Liebigs. Ann. Chem.*, (1975)145.
[27] *Yukikinzoku no Kagaku to Ooya*, Kinki Kagaku Kogyokai ed., Asakura Shoten, p. 157, 1962.

[28] Y. Yamamoto and Y. Naruta, *Yuki Kinzoku Kagaku*, Maruzen, Tokyo, p. 29, 1983.

[29] R.A. Andersen and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, (1977)809.

[30] G.E. Coates and J.A. Heslop, *J. Chem. Soc. (A)*, (1968)514.

[31] W. Strohmeier and F. Seifert, *Chem. Ber.*, **94** (1961) 2356.

[32] C.W. Kamienski and J.F. Eastham, *J. Org. Chem.*, **34** (1969) 1116.

[33] B. Denise, J.-F. Fauvarque and J. Ducom, *Tetrahedron Lett.*, (1970)335.

[34] H.C. Holtkamp, C. Blomberg and F. Bickelhaupt, *J. Organomet. Chem.*, **19** (1969) 279.

[35] C.W. Kamienski and J.F. Eastham, *J. Organomet. Chem.*, **8** (1967) 542.

[36] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **49** (1927) 2328.

[37] P.R. Markies, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets and A.L. Speck, *Adv. Organomet. Chem.*, **16** (1977) 147.

[38] Ch. Elschenbroich and A. Salzer, *Organometalllics*, VCH, Weinheim, p. 40, 1989.

[39] J. Lifschitz and O.E. Kalberer, *Z. Phys. Chem.*, **102** (1922) 393.

[40] G. Stucky and R.E. Rundle, *J. Am. Chem. Soc.*, **86** (1964) 4825.

[41] L.J. Guggenberger and R.E. Rundle, *J. Am. Chem. Soc.*, **86** (1964) 5344.

[42] L.J. Guggenberger and R.E. Rundle, *J. Am. Chem. Soc.*, **90** (1968) 5375.

[43] J. Toney and G.D. Stuckey, *J. Chem. Soc. Chem. Commun.*, (1967)1168.

[44] P.R. Markies, R.M. Altink, A. Villena, O.S. Akkerman and F. Bickelhaupt, *J. Organomet. Chem.*, **402** (1991) 289.

[45] P.R. Markies, G. Schat, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, A.J.M. Duisengerg and A.L. Speck, *J. Organomet. Chem.*, **375** (1989) 11.

[46] P.R. Markies, G. Schat, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, P. van der Sluis and A.L. Speck, *J. Organomet. Chem.*, **393** (1990) 315.

[47] W.A. Barber, *Inorg. Syn.*, **6** (1960) 11.

[48] A. Haaland, J. Lusztyk, J. Brunvoll and K.B. Starowieyski, *J. Organomet. Chem.*, **85** (1975) 279.

[48a] S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, A.J. Jagger and J.D. Smith, *J. Organomet. Chem.*, **469** (1994) 129.

[48b] E. Weiss, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 1501.

[49] J.H. Woltiz, C.A. Hollingsworth and R. Dessy, *J. Am. Chem. Soc.*, **77** (1955) 103.

[50] B.J. Wakefield, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel eds., Pergamon Press, Oxford, vol. 7, p. 1, 1982

[51] *Jikken Kagaku Koza 25*, 4th ed., Maruzen, Yuki Gosei VII, p. 59, 1991.

[52] H. Gilman and J. Eisch, *J. Am. Chem. Soc.*, **79** (1957) 2150.

[53] E.L. Eliel, J.K. Koshimies and B. Lohri, *J. Am. Chem. Soc.*, **100** (1978) 1614.

[54] J. Tsuji *Yuki Gosei okaeta Sen-i Kizoku (Transition Metals in Organic Synthesis)*, Kagaku Dojin, pp. 35, 105, 123, (1991).

[55] T. Kohei and M. Kumada, *Kagaku*, **30** (1975) 832.

[56] K. Tamao, M. Kumada, S. Akutagawa and S. Otsuka, *Kagaku no Ryoiki, Zokan*, **117** (1977) 45.

[57] K. Tamao, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.*, **94** (1972) 4374.

[58] K. Tamao, Y. Kiso, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.*, **94** (1972) 9268.

[59] Y. Kiso, K. Tamao, and M. Kumada, *J. Organomet. Chem.*, **50** (1973) C12.

[60] K. Tamao, M. Zenbayashi, Y. Kiso and M. Kumada, *J. Organomet. Chem.*, **55** (1973) C91.

[61] M. Zembayashi, K. Tamao and M. Kumada, *Tetrahedron Lett.*, (1975)1719.

[62] K. Tamao, A. Minato, N. Miyake, T. Matsuda and M. Kumada *Chem. Lett*, (1975)133.

[63] M. Kumada, *Organotransition-Metal Chemistry*, Y. Ishii and M. Tsutsui, ed., Plenum, New York, p. 211, 1975.

[64] M. Zembayashi, K. Tamao, T. Hayashi, T. Mise and M. Kumada, *Tetrahedron Lett.*, (1977)1799.

[65] K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyake, T. Hayashi and M. Kumada, *Tetrahedron Lett.*, (1977)1389.

[66] K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato and M. Kumada, *Bull. Chem. Soc. Japan*, **49** (1976) 1958.

[67] T. Hayashi and M. Kumada, *Fundamental Research in Homogeneous Catalysis*, Y. Ishii and M. Tsutsui, ed., vol. 2, Plenum, New York, p. 159, 1978.

[68] T. Hayashi, M. Konishi and M. Kumada, *Tetrahedron Lett.*, (1979)1871.

[69] K. Tamao, T. Hayashi, H. Matsumoto, H. Yamamoto and M. Kumada, *Tetrahedron Lett.*, (1979)2115.

[70] H. Hayashi, M. Fukushima, M. Konishi and M. Kumada, *Tetrahedron Lett.*, (1980)79.

[71] T. Hayashi, K. Kanehira, T. Hioki and M. Kumada, *Tetrahedron Lett.*, (1981)137.

[72] A. Minato, K. Tamao, T. Hayashi, K. Suzuki and M. Kumada, *Tetrahedron Lett.*, (1980)845.

[73] T. Hayashi, Y. Katsuro and M. Kumada, *Tetrahedron Lett.*, (1980)3915.

[74] A. Minato, K. Tamao, K. Suzuki and M. Kumada, *Tetrahedron Lett.*, (1980)4017.

[75] T. Hayashi, M. Konishi and M. Kumada, *J. Organomet. Chem.*, **186** (1980) C1.

[76] T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto and M. Kumada, *Bull. Chem. Soc. Japan*, **53** (1980) 1138.

[77] T. Hayashi, M. Konishi, K. Yokota and M. Kumada, *Chem. Lett.* (1980)767.

[78] M. Kumada, *Pure Appl. Chem.*, **52** (1980) 669.

[79] T. Hayashi, Y. Katsuro, Y. Okamoto and M. Kumada, *Tetrahedron Lett.*, (1981) 4449.

[80] T. Hayashi, M. Konishi, T. Hioki, M. Kumada, A. Patajczak and H. Niedbala, *Bull. Chem. Soc. Japan*, **54** (1981) 3615.

[81] T. Hayashi, T. Fujiwa, Y. Okamoto, Y. Katsuro and M. Kumada, *Synthesis*, (1981) 1001.

[82] K. Tamao, S. Kodama, I. Nakajima and M. Kumada, *Tetrahedron Lett.*, (1982)3347.

[83] T. Hayashi, M. Konishi, M. Fukushima, T. Mise, M. Kagotani, M. Tajika and M. Kumada, *J. Am. Chem. Soc.*, **104** (1982) 180.

[84] M. Kumada, T. Hayashi and K. Tamao *Fundamental Research in Organometallic Chemistry*, M. Tsutsui, Y. Ishii and H. Yaozeng, eds., Van Norstrand Reinhold, New York, p. 175, 1982.

[85] H. Hayashi and M. Kumada, *Acc. Chem. Res.*, **15** (1982) 395.

[86] T. Hayashi, T. Hagihara, Y. Katsuro and M. Kumada, *Bull. Chem. Soc. Japan*, **56** (1983) 363.

[87] K. Tamao, T. Iwahara, R. Kanatani and M. Kumada, *Tetrahedron Lett.*, (1984)1909.

[88] T. Hayashi, M. Kumada, *Asymmetric Synthesis*, J.D. Morrison ed., vol. 5, Academic Press, New York, p. 147, 1985.

[89] Y. Kiso, K. Tamao, N. Miyake, K. Yamamoto and M. Kumada, *Tetrahedron Lett.*, (1974)3.

[90] T. Hayashi, M. Tajika, K. Tamao and M. Kumada, *J. Am. Chem. Soc.*, **98** (1976) 3718.

[91] T. Hayashi, N. Nagashima and M. Kumada, *Tetrahedron Lett.*, (1980)4623.

[92] T. Hayashi, M. Konishi, M. Fukushima, K. Kanehira, T. Hioki and M. Kumada, *J. Org. Chem.*, **48** (1983) 2195.

[93] T. Hayashi, M. Konishi, H. Ito and M. Kumada, *J. Am. Chem. Soc.*, **104** (1982) 4962.

[94] T. Hayashi, M. Konishi and M. Kumada, *J. Org. Chem.*, **48** (1983) 281.

[95] T. Hayashi, Y. Okamoto and M. Kumada, *Tetrahedron Lett.*, (1983)807.

[96] T. Hayashi, K. Kanehira, H. Tsuchiya and M. Kumada, *J. Chem. Soc. Chem. Commun.*, (1982)1162.

[97] L. Friedman and A. Shani, *J. Am. Chem. Soc.*, **96** (1974) 7101.

[98] K. Tamao, S. Kodama, T. Nakatsuka, Y. Kiso and M. Kumada, *J. Am. Chem. Soc.*, **97** (1975) 4405.
[99] M. Kumada, unpublished review.
[100] T. Takahashi, T. Seki, Y. Nitto and M. Saburi, *J. Am. Chem. Soc.*, **113** (1991) 6266.
[101] K.S. Knight and R.M. Waymouth, *J. Am. Chem. Soc.*, **113** (1991) 6268.

5 Organozinc Compounds

5.1 INTRODUCTION

Zinc is an element used for sheet metal, a zinc flower for white pigments (zinc oxide) and dry battery materials, etc. Organozinc compounds, as described in Chapter 2, play the most important part as reagents for organic syntheses until Grignard reagents were found in 1900. But after that the Grignard reagents replaced organozinc compounds. However, the organzinc compounds have been formed to have different characteristics from reactive Grignard reagents and organolithium compounds. Furthermore, various kinds of new organosynthetic methods have been developed by adding palladium, nickel and copper compounds as the catalysts to the organic compounds. Therefore, recently attention to organozinc compounds has returned.

5.2 ZINC

Zinc is an element of group 12 of the periodic table, of which the outer electrons are $3d^{10}4s^2$ and zinc is in the same group of elements, such as Cd and Hg. Zinc exists as 70 ppm in the Earth's crust and exists in similar amounts to Cr (100 ppm) and Ni (80 ppm) [1]. Zinc is produced from sphalerite (ZnS) as ores. There are two processes, a dry process and a wet process, for the refinement of zinc. However, zinc is largely produced by the wet process. The wet process is equally to be said as an electrolysis process. The sphalerite contains lead, iron cadmium and copper, etc. besides zinc and, by a flotation separation of the ores, the zinc concentrate (50–55 % Zn) and the lead concentrate are separated. The zinc concentrate is burnt and put into a vessel and dissolved in an electrolysis foul solution. The zinc sulfate solution and concentrated mud (the common name is red mud) are separated by a filter. Cadmium and copper, etc., as impurities dissolve in the zinc sulfate solution. Then zinc dust is added to the solution to precipitate these impurities to form a clean solution of zinc sulfate to be electrolyzed. In the electrolysis, lead containing 1 % of silver is used as a cathode and aluminum is used as an anode, and zinc is produced on the cathode [2–4]. The properties of zinc are shown in Table 5.1.

Zinc is easily corrodable metal in air, but the corrosion is inhibited by the oxide layer on the surface. Zinc burns easily in the air on heating. Zinc directly reacts with chlorine and sulfur, and it dissolves in an acid or alkali solution to generate hydrogen. Zinc does not dissolve in water. However, in the presence of oxygen, it

Table 5.1 Properties of zinc [5–7]

Property	Value
melting point, °C	419.5
boiling point, °C	907
crystal structure	hexagonal closed-packed
density at 25 °C, g/cm^3	7.133
linear coefficient of thermal expansion at 20 °C, K^{-1}	0.530×10^{-4}
electrical resistivity at 20 °C, μΩ·cm	5.80
hardness Mohs scale	2.5
thermal conductivity, Wm^{-1}K^{-1}, at 18 °C	113.0
mass susceptibility, cm^{3}g^{-1}	9.0×10^{-6}
ionic radius, Zn^{2+}, nm	0.074
covalent radium, nm	0.131
metallic radius, nm	0.138

gradually reacts with water to give zinc hydroxide ($Zn(OH)_2$) and peroxide. With aqueous potassium cyanide solution and aqueous ammonia solution, zinc forms its complexes and dissolves in these solutions.

Zinc forms, usually Z^{2+} and Z^{2+}, have the tetrahedral structure of four-coordination. Zinc is an indispensable element in organisms, and twenty or more kinds of enzymes contain zinc. A human being contains two to three grams of zinc [2–9]. Zinc is used as an iron sheet covered with zinc (zinc sheet), a zinc plate, a brass, a zinc diecast (a zinc alloy which has good cutting processability), a zinc plate for phototype process, a zinc plate for dry battery, a zinc flower for white pigment and fireworks, etc. [2–9].

5.3 PREPARATION OF ORGANOZINC COMPOUNDS

Organozinc compounds are prepared primarily by the following three reactions.

(1) Direct reactions
(2) Reactions with various kinds of organometallic compounds
(3) Others

5.3.1 DIRECT REACTIONS

Organozinc compounds were first prepared in 1849 by the reaction shown in eq. (5.1) by Frankland [10]. Copper is preferable for the catalyst. The alloy of zinc containing 5–10 % of copper is used for this reaction [11–13]. Sodium and silver are also available for the catalyst [12].

$$\mathrm{EtI} \quad + \quad \mathrm{Zn} \xrightarrow{90-200\ ^{\circ}\mathrm{C},\ 2\ \mathrm{hr}} \mathrm{EtZnI} \tag{5.1}$$

The direct reaction of organic halide with zinc, shown in eq. (5.1), proceeds with active zinc in the absence of the metal catalyst. Two processes for the activation of zinc are exploited [14–17]. The first process is the reduction of zinc halide with organoalkali metal compounds. For example, $ZnCl_2$ is reduced by naphthalene-lithium. The second process is the irradiation by ultrasound [16,17].

The direct reaction shown in eq. (5.1) is similar to the reaction which is applied for organosilicon compounds and organotin compounds in industrial preparations. The alkylzinc halides obtained give dialkylzinc by distillation with heating as shown in eq. (5.2) [12]. Usually primary and secondary iodides and a mixture of bromides and iodides are used for the direct reactions.

$$2\mathrm{RZnX} \longrightarrow \mathrm{R_2Zn} \quad + \quad \mathrm{ZnX_2} \tag{5.2}$$

5.3.2 REACTIONS WITH VARIOUS KINDS OF ORGANOMETALLIC COMPOUNDS

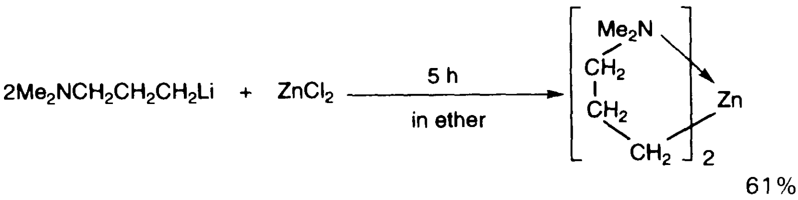
As shown in eqs. (5.3)–(5.7), organozinc compounds are easily prepared by the reactions of zinc compounds or zinc metal with organometallic compounds such as Grignard reagents, organoaluminum compounds, organomercury compounds and organolithium compounds [12,13,18].

$$2\mathrm{CH_2{=}CHCH_2MgBr} \quad + \quad \mathrm{ZnCl_2} \xrightarrow[\text{in ether}]{} \underset{30\ \%}{(\mathrm{CH_2{=}CH\text{-}CH_2})_2\mathrm{Zn}} + 2\mathrm{MgBrCl} \tag{5.3}$$

$$2\mathrm{CH_2{=}CHMgBr} \quad + \quad \mathrm{ZnCl_2} \xrightarrow[\text{in THF}]{55\ ^{\circ}\mathrm{C},\ 12\ \mathrm{h}} \underset{10\ \%}{(\mathrm{CH_2{=}CH})_2\mathrm{Zn}} + 2\mathrm{MgBrCl} \tag{5.4}$$

$$2\mathrm{Me_3Al} \quad + \quad \mathrm{Zn(OAc)_2} \xrightarrow[\text{in decaline}]{10\ ^{\circ}\mathrm{C},\ 2\ \mathrm{h}} \underset{88\ \%}{\mathrm{Me_2Zn}} \quad + \quad 2\mathrm{Me_2AlOAc} \tag{5.5}$$

$$\mathrm{Ph_2Hg} \quad + \quad \mathrm{Zn} \xrightarrow[\text{in xylene}]{\text{heat, ca. 1 h}} \underset{70\ \%}{\mathrm{Ph_2Zn}} \quad + \quad \mathrm{Hg} \tag{5.6}$$



(5.7)

5.3.3 OTHERS

The other reactions are decarboxylations, and reactions with reactive amines, salts, etc. The decarboxylation gives organozinc compounds by heating carboxylic acid salts as shown in eq. (5.8) [19].

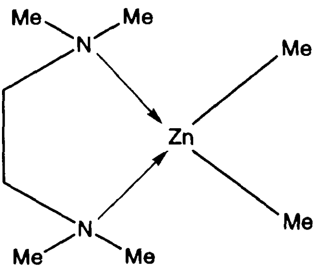
$$(C_6F_5COO)_2Zn \xrightarrow{220\ ^\circ C\ /\ 10^{-2}\ mmHg} \underset{\substack{mp\ 106-108\ ^\circ C \\ 62\ \%}}{(C_6F_5)_2Zn} + 2CO_2 \qquad (5.8)$$

Moreover, since $Zn(NSiMe_3)_2$ is reactive, it is able to react with cyclopentadiene directly to give cyclopentadienylzinc in high yield as shown in eq. (5.9) [13,20].

$$Zn[N(SiMe_3)_2]_2 + 2CpH \xrightarrow[\text{in ether}]{\text{room temp, 1 h}} \underset{90\ \%}{Cp_2Zn} + 2HN(SiMe_3)_2 \qquad (5.9)$$

5.4 STRUCTURES OF ORGANOZINC COMPOUNDS

Organozinc compounds have been found by X-ray diffraction studies to form primarily the tetrahedral structure of four-coordination stabilized by the coordination of lone pair electrons of nitrogen or oxygen as shown in Figure 5.1 [21–28].



pseudo-tetrahedral coordination

Figure 5.1 Structure of $Me_2Zn(Me_2NCH_2CH_2NMe_2)$ [22].

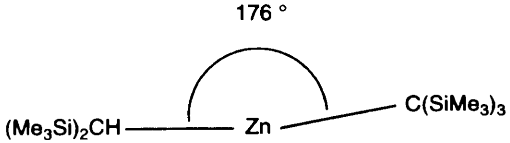


Figure 5.2 Structure of $(Me_3Si)_2CH–Zn–C(SiMe_3)_3$ [29]

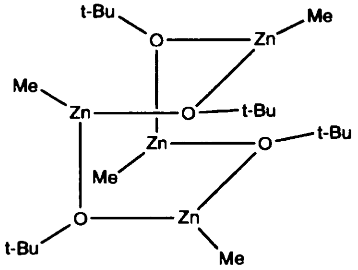


Figure 5.3 Structure of $(MeZnO\text{-}t\text{-}Bu)_4$ [30].

Subsequently, a linear structure of two coordination was found as shown in Figure 5.2 [29]. However, these structures change to the distorted tetrahedral structures or linear structures if they can form ring structures or they have a bulky organic group.

The others are three-coordination structures as shown in Figure 5.3 [30–32]. The compound shown in Figure 5.4 is the four-coordination structure; however, when

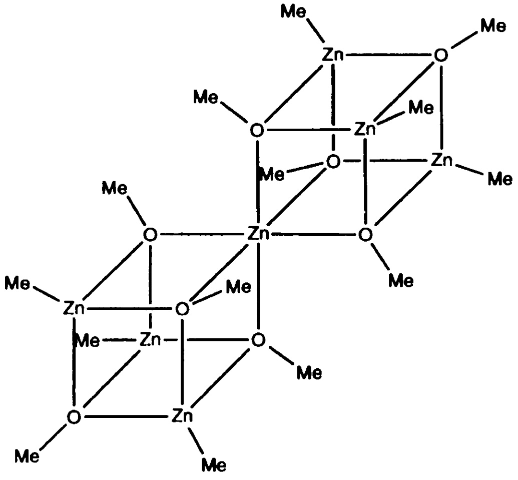


Figure 5.4 Structure of $Me_6Zn_7(OMe)_8$ [33].

the zinc atom is bonded with only oxygen atoms, the octahedral structure of six coordination is [33,34].

5.5 REACTIONS OF ORGANOZINC COMPOUNDS

Organozinc compounds are low reactivity compounds in comparison with Grignard reagents and organolithium compounds described above. However, the selectivity of their reactions is high. Hence, organozinc compounds are utilized as highly selective organosynthetic reagents with highly reactive organic compounds. In particular, as the reactivity of organic compounds with a functional group is high, the desired compounds tend to be obtained by reactions with organozinc compounds. In contrast, Grignard reagents and organolithium compounds are often too reactive and they react directly with functional groups; therefore, in general, it is difficult to get the desired compounds in such reactions.

Organozinc compounds, as described above, become highly reactive by using catalysts such as palladium, nickel and copper compounds. Therefore, even if the reaction could not proceed since the reactivity of the organozinc compound is too low, it is able to be carried out. Recently, these reactions using catalysts are noted because the selectivity of the reaction is high [15,35–47].

5.5.1 TRANSMETALATIONS

Grignard reagents or organolithium compounds are usually used for the syntheses of organometallic compounds. However, with some organometallic compounds, Grignard reagents or organolithium compounds are too reactive, and for the syntheses of organozinc compounds are available for these reactions. For example, organosilver compounds and organocopper compounds, as shown in eqs. (5.10) and (5.11), organozinc compounds are used [12,48,49].

$$\mathrm{Ph_2Zn} + \mathrm{AgNO_3} \xrightarrow[\text{in ether}]{0\ ^\circ\mathrm{C},\ 2\ \mathrm{h}} \underset{93\ \%}{\mathrm{PhAg}} + \mathrm{PhZnNO_3} \quad (5.10)$$

$$\mathrm{Me_2Zn} + 2\mathrm{CuCl} \xrightarrow[\text{in ether}]{-70\ ^\circ\mathrm{C},\ 4\ \mathrm{h}} 2\mathrm{MeCu} + \mathrm{ZnCl_2} \quad (5.11)$$

almost quantitative yield

The other examples are organotantalum, organoniobium and organovanadium compounds, as shown in eq. (5.12)–(5.14) [50,51].

$$\tfrac{3}{2}(Me_3SiCH_2)_2Zn + TaCl_5 \xrightarrow[\text{in ether}]{\text{room temp, 4 h}} \underset{77\ \%}{(Me_3SiCH_2)_3TaCl_2} \tag{5.12}$$

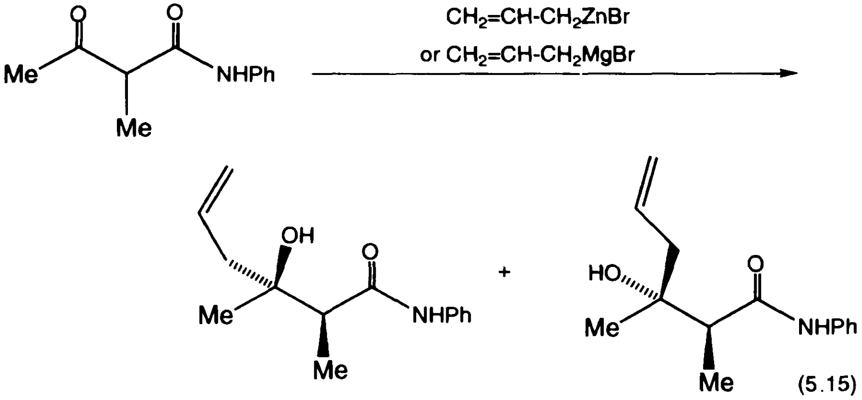
$$\tfrac{3}{2}(Me_3SiCH_2)_2Zn + NbCl_5 \xrightarrow[\text{in ether}]{\text{room temp, 4 h}} \underset{53\ \%}{(Me_3SiCH_2)_3NbCl_2} \tag{5.13}$$

$$Me_2Zn + VO(OR)_3 \xrightarrow[\text{in hexane}]{-70\ ^\circ\text{C, 4 h}} MeV(OR)_2 + MeZnOR \tag{5.14}$$

R = Me, Et, *i*-Pr, *s*-Bu, *t*-Bu

5.5.2 ADDITIONS

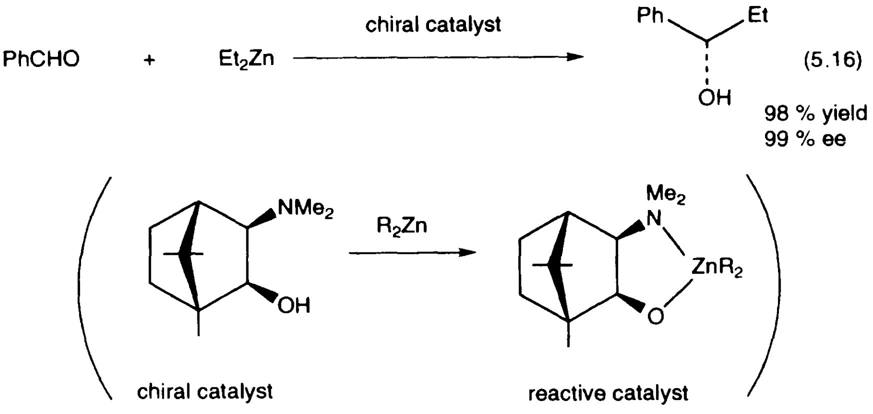
With organozinc compounds, highly selective additions to the carbonyl compounds such as ketones proceed, which is different from Grignard and organolithium compounds. For example, the stereoselectivity of the addition of an oxoamide with organozinc compounds is higher than that of the reaction with Grignard reagents as shown in eq. (5.15) [52].



(5.15)

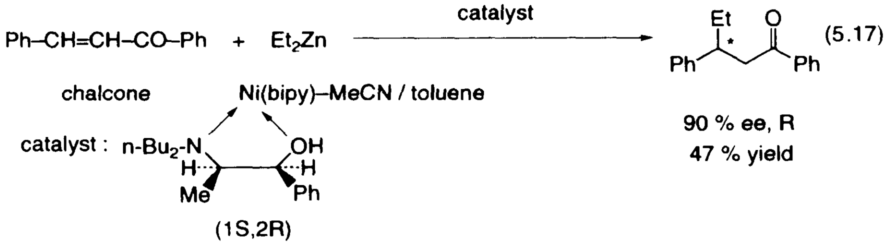
CH_2=CH-CH_2ZnBr :	>99 %	:	< 1%
CH_2=CH-CH_2MgBr :	80 %	:	20 %

Examples of the reaction with aldehydes are few since the reactivity of organozinc compounds is low. Recently, the articles about these reactions have increased by the improvement of the reactivity by means of the use of coordination compounds, irradiation of ultrasound, and transition metal catalysts, etc. For example, as shown in eq. (5.16), with a chiral coordination compounds, the reactivity of organozinc compounds is improved by the coordination to the metal to show a high stereospecificity [28,36,38,53–61]. For example, Me_2Zn has a linear



structure as shown in Figure 5.2. The bond length of Zn–C (Me) is about 1.90 Å [61a] and Me_2Zn is not able to add to an aldehyde. However, the dialkylzincs bonded with amino compounds, which form a bidentate coordination as shown in eq. (5.16), are able to react. The zinc forms a tetrahedral structure of four coordination as shown in Figure 5.1. Then the bond length of Zn–C becomes slightly longer (for example, Zn–C of $Me_2Zn(Me_2NCH_2CH_2NMe_2)$ is 1.98 Å [22]. Namely, the energy of the Zn–C bond decreases and the nucleophilicity of the methyl group increases. Then, by using chiral amino compounds, highly reactive chiral organozinc compounds form and the reaction gives the chiral alcohols [12].

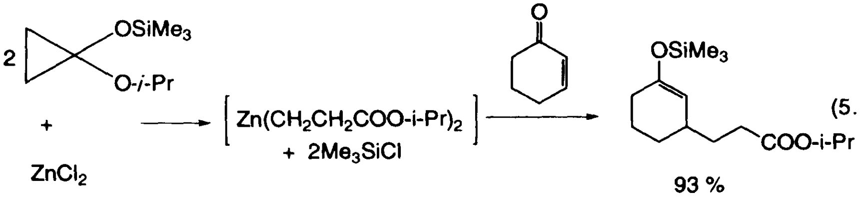
With organozinc compounds in the presence of palladium, nickel or copper compounds as the catalysts, highly selective additions to carbonyl groups or carbon–carbon double bonds proceed. For example, an addition of chalcone (Ph-COCH=CH-Ph) proceeds with dialkylzinc in the presence of a nickel catalyst. The asymmetric addition proceeds by using a nickel catalyst having the chiral ligand as shown in eq. (5.17) [38,43].



Alkoxysiloxycyclopropanes react with $ZnCl_2$ to give $Zn(CH_2CH_2COOR)_2$. This organozinc compound has a larger number of carbon atoms, by one, than the Reformatsky reagent ($XZnCH_2COOR$) described in the next section. Then it is a Remote Reformatsky reagent-like β-ester.


(5.18)

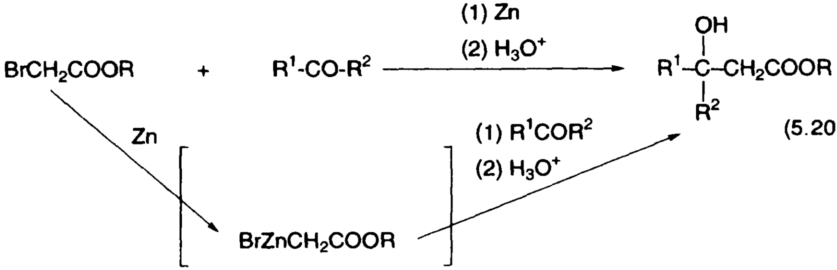
For example, the alkoxycarbonylethyl compound is easily obtained by addition reaction of the β-ester with an unsaturated compound as shown in eq. (5.19) [62,63].


(5.19)

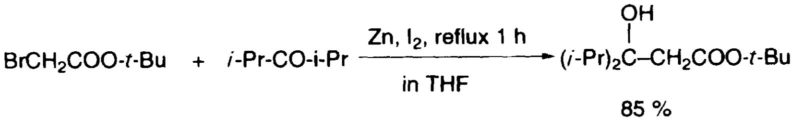
5.5.3 REFORMATSKY REACTIONS

The Reformatsky reaction is one of the representative reactions of zinc being used as a catalysts [12,35–38,41,64–74]. The Reformatsky reaction is that reaction with α-haloesters, carbonyl compounds and zinc that produces β-hydroxyester as shown in eq. (5.20). The reaction of α-haloesters with zinc yields organozinc compounds ($XZnCH_2COOR$) which are called the Reformatsky reagents. These Reformatsky reagents are the organozinc compounds which are considered to be the intermediates of the Reformatsky reaction.

If the carbonyl compounds tend to be easily reduced, firstly, the Reformatsky reagents are synthesized in advance, and then these reagents react with carbonyl compounds [36].


(5.20)

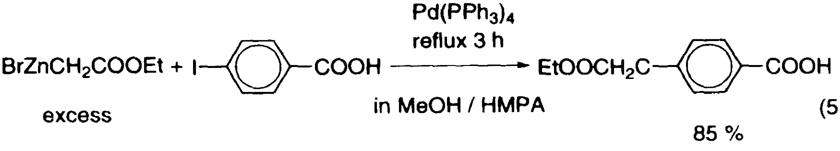
Aldehydes are used besides ketones as shown in eq. (5.21) as the carbonyl compounds of the Reformatsky reactions. Furthermore, α-haloamides, α-halonitrile, alkyl halides and propagyl halides besides α-haloesters are used as the reagents of Reformatsky reactions [35,72].



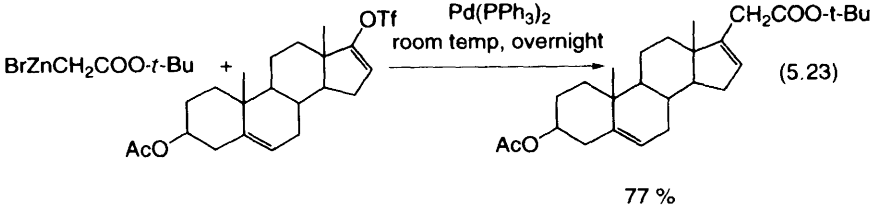
$$\mathrm{BrCH_2COO\text{-}}t\mathrm{\text{-}Bu} + i\mathrm{\text{-}Pr\text{-}CO\text{-}i\text{-}Pr} \xrightarrow[\text{in THF}]{\text{Zn, I}_2\text{, reflux 1 h}} (i\mathrm{\text{-}Pr})_2\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{\text{-}CH_2COO\text{-}}t\mathrm{\text{-}Bu} \quad (5.21)$$

85 %

With Reformatsky reagents in the presence of palladium compounds or nickel compounds as the catalysts, an arylation, a vinylation and a cyclization reaction proceed [41]. For example, the arylation and the vinylation reactions are shown in eqs. (5.22) and (5.23), respectively [73,74].

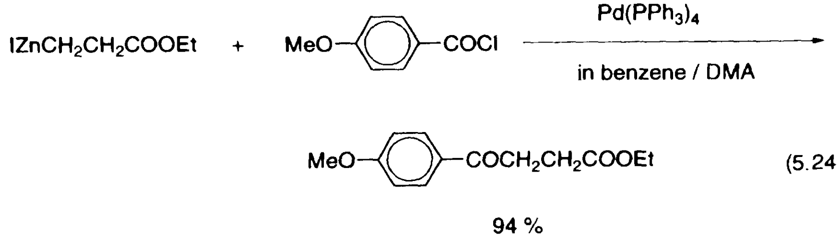


(5.22)



(5.23)

The Reformatsky reagents are the compounds of a α-haloester with zinc. Further, with the compounds of β- or γ-haloester with zinc the coupling reactions are able to proceed in the presence of catalysts such as palladium, copper and nickel compounds. These reactions are called the Remote Reformatsky reactions. For example, the reaction with palladium catalyst is shown in eq. (5.24) [42].



(5.24)

5.5.4 ZAITSEV REACTIONS

Zaitsev reactions are the reaction that organic halides such as allyl halides, benzyl halides and propagyl halides react with aldehydes or ketones in the presence of zinc, and the product is hydrolyzed to give secondary or tertiary alcohols as shown in eq. (5.25)

$$\mathrm{RCH{=}CH\text{-}CH_2X + R^1COR^2 + Zn \longrightarrow RCH{=}CH\text{-}CH_2CR^1R^2OH} \quad (5.25)$$

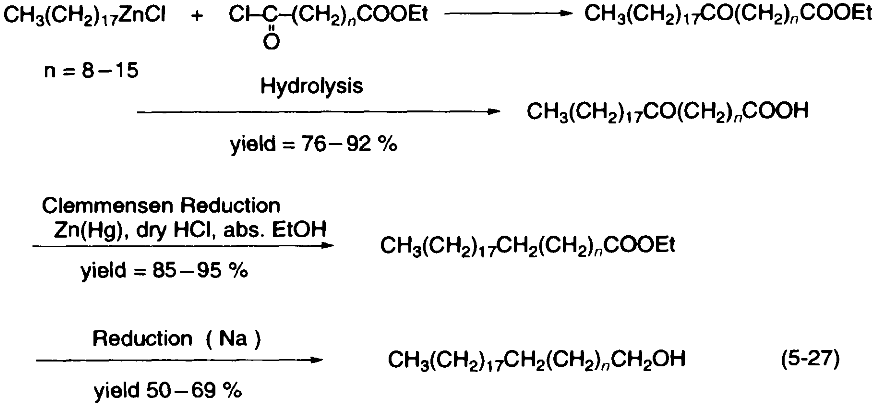
Zaitsev reactions also proceed similar to the Reformatsky reactions. Namely, organozinc compounds are synthesized in advance, and subsequently they react with aldehydes or ketones. Therefore, addition to the carbonyl of arylzinc compounds as shown in eq. (5.15) is also known as the Zaitsev reaction. Not only the addition to the carbonyl group of aldehydes or ketones but also the addition to carbon–carbon double bonds are the related reactions of Zaitsev reactions as shown in eq. (5.26) [37].

$$\mathrm{CH_2{=}CHCH_2ZnBr + CH_2{=}CH(CH_2)_nNEt_2 \longrightarrow}$$

$$\mathrm{CH_2{=}CHCH_2CH_2CH_2(CH_2)_nNEt_2 + CH_2{=}CHCH_2CH(CH_3)(CH_2)_nNEt_2} \quad (5.26)$$

5.5.5 COUPLING REACTIONS

The Reformatsky and Zaitsev reactions described in the previous sections are the primary coupling reactions with zinc metal. This section shows the coupling reaction between organozinc compounds and organic halides. With organozinc compounds, various kinds of coupling reactions proceed as shown in eqs. (5.27)–(5.29) [75]. In particular, acyl halides easily react with organozinc compounds to give the ketones in high yields, and furthermore the ketones are reduced to give the long chain primary alcohols as shown in eq. (5.27) [36,76,76a].

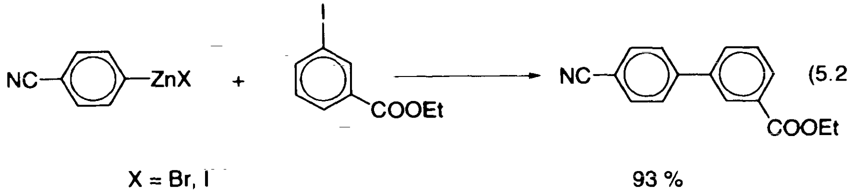


$$\mathrm{CH_3(CH_2)_{17}ZnCl + Cl\text{-}\underset{\displaystyle\overset{\|}{O}}{C}\text{-}(CH_2)_nCOOEt \longrightarrow CH_3(CH_2)_{17}CO(CH_2)_nCOOEt}$$

$$n = 8-15 \qquad \xrightarrow[\text{yield = 76−92 \%}]{\text{Hydrolysis}} \mathrm{CH_3(CH_2)_{17}CO(CH_2)_nCOOH}$$

$$\xrightarrow[\text{yield = 85−95 \%}]{\substack{\text{Clemmensen Reduction}\\ \text{Zn(Hg), dry HCl, abs. EtOH}}} \mathrm{CH_3(CH_2)_{17}CH_2(CH_2)_nCOOEt}$$

$$\xrightarrow[\text{yield 50−69 \%}]{\text{Reduction (Na)}} \mathrm{CH_3(CH_2)_{17}CH_2(CH_2)_nCH_2OH} \quad (5\text{-}27)$$



(5.28)

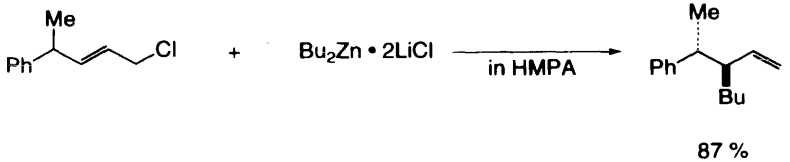
$$(E)\text{-NC(CH}_2)_3\text{(H)C=C(H)ZnX} \quad + \quad (E)\text{PivO(CH}_2)_3\text{(H)C=C(H)I} \xrightarrow{\text{catalyst}}$$

$$(E,E)\text{-NC(CH}_2)_3\text{(H)C=C(H)(H)C=C(H)(CH}_2)_3\text{OPiv} \qquad (5.29)$$

86 %

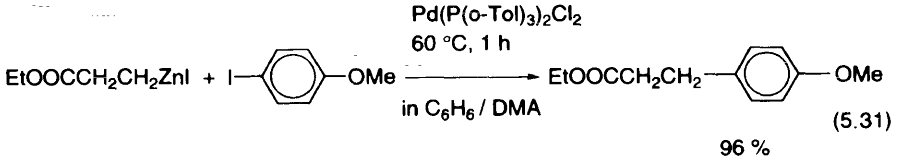
catalyst = Pd(dba) (4 mol %) + PPh_3 (16 mol %)
dba = Ph-CH=CH-CO-CH=CH-Ph
PivO = $(CH_3)_3CCO$

Further, as shown in eq. (5.30), in the presence of lithium halides, the highly stereospecific S_N2' reactions of halides with organozinc compounds proceed [77].



(5.30)

Since transmetalation of organozinc halides in the presence of palladium or nickel compounds easily proceeds, the coupling reaction is carried out by the catalytic reaction via formation reaction of these organometallic compounds. For example, an aromatic β-ester is prepared in a high yield by a reaction with a palladium catalyst as shown in eq. (5.31) [78].



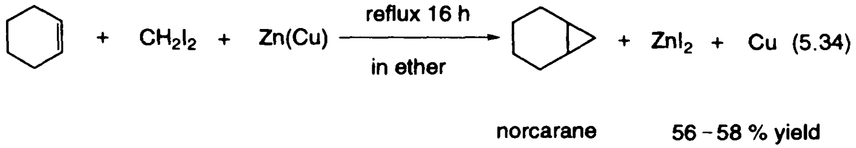
5.6 SIMMON–SMITH REACTIONS

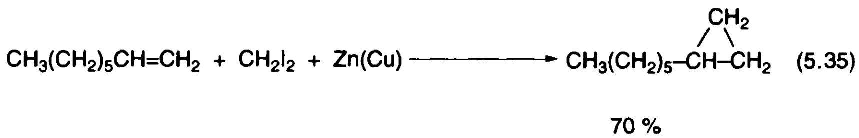
Organozinc compounds, XZnCRR′ (RR′ = H, alkyl, X = halogen), are widely used for the synthesis of cyclopropanes as Simmon–Smith reagents [12,36,37,79–93]. Simmon–Smith reagents are prepared by two processes as shown in eqs. (5.32) and (5.53). The first one is the reaction of diazomethane with zinc halides. The second is the reaction of methylene iodide with an activated zinc. Zinc containing 10% of copper is mainly available as the activated zinc. A zinc–copper couple obtained by reduction of the mixture of zinc powder and copper oxide with hydrogen at 500 °C, is also the activated zinc [81–83].

$$ZnX_2 + CH_2N_2 \longrightarrow XZnCH_2X + N_2 \qquad (5.32)$$

$$Zn / Cu + CH_2I_2 \longrightarrow IZnCH_2I \qquad (5.33)$$

Simmon–Smith reactions are accelerated by oxygen, radical initiators and UV irradiation. All additions are stereospecific. Hence, it is considered that free carbene does not exist in the reactions. The reaction mechanism is not known. Simmon–Smith reactions are shown in eq. (5.34) and (5.35). The active zinc metal is usually used for Simmon–Smith reactions, but organozinc compounds are able to be used in place of the active zinc metal.

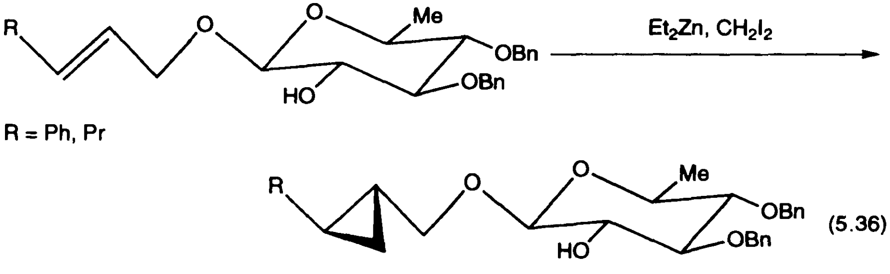




$$CH_3(CH_2)_5CH{=}CH_2 + CH_2I_2 + Zn(Cu) \longrightarrow CH_3(CH_2)_5\text{–}\overset{CH_2}{CH\text{–}CH_2} \qquad (5.35)$$

70 %

By using EtZnI in place of zinc metal in the Simmon–Smith reactions, the yields are improved from 56–58 % to 92 % for the reaction of cyclohexene as shown in eq. (5.34) and from 70 % to 77 % for the reaction of *n*-hexene shown in eq. (5.35) [87]. The reaction with Et_2Zn is shown in eq. (5.36) [92].



yield ≥ 97 %
diastereoselectivities ≥ 50 : 1

5.7 OTHERS

One of the other reactions with organozinc compounds are insertion reactions to sulfur dioxide or oxygen. For example, dialkylzinc reacts with sulfur dioxide to give almost quantitatively an insertion product to the zinc–carbon bond as shown in eq. (5.37) [94].

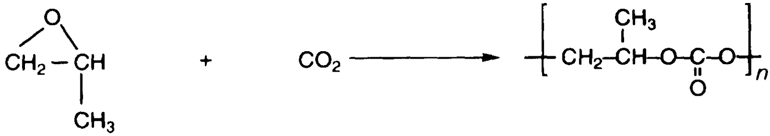
$$Me_2Zn \quad + \quad SO_2 \xrightarrow{\qquad\qquad} MeZnOSOMe \qquad (5.37)$$

Organozinc compounds cause autoxidation to yield the zinc peroxides. They explode in pure oxygen. The organozinc compounds react with oxygen in ether. In the case of diethylzinc, as shown in eq. (5.38), at first the peroxide is produced, and then the peroxide reacts with the unreacted diethylzinc to yield an alkoxide [95].

$$Et_2Zn + O_2 \xrightarrow{\qquad\qquad} EtOOZnEt \xrightarrow{Et_2Zn} Zn(OEt)_2 \qquad (5.38)$$

Organozinc compounds are available for polymerization catalysts. Many studies of the stereospecific polymerization of olefins such as ethylene, propylene and styrene in the presence of combination catalysts of especially R_2Zn and $TiCl_4$ have been reported [12,37].

Enoue *et al.* in 1968, first prepared highly polymeric polycarbonate by polymerization of epoxy with zinc compounds such as Et_2Zn as the catalysts [96–100]. The polymer is stable up to 180°C [96]. Polycarbonate of epoxide with carbon dioxide has been industrially produced from PAC Polymer Company [96]. Since the polycarbonates are biodegradable polymers, they have been investigated as release sustaining materials for drugs [101].



(5.39)

REFERENCES

[1] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
[2] *12695 no Kagaku Shohin*, Kagaku Kogyo Nipposha, Tokyo, p. 45, 1995.
[3] *Kagaki Binran Ooyohen*, 3rd ed., Japan Chemical Society ed., p. 262, 1980.
[4] *Kino Zairyo*, **14** (1994) 56.
[5] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., John Wiley, New York, vol. 24, p. 807, 1980.
[6] *Kagaku Daijiten*, Tokyo Kagaku Doojin, Tokyo, p.6, 1989.

[7] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, 4th ed., p. 4, 1987.
[8] *Sekai Dai Hyakkajiten*, Heibonsha, Tokyo, vol. 1, p. 64, 1988.
[9] *Sekai Kagaku Daijiten, Technopia (Encyclopedia of Science and Technology)*, Kodansha, Tokyo, vol. 1, p. 6, 1977.
[10] E. Frankland, *Liebigs Ann. Chem.*, **71** (1848) 171.
[11] E.G. Rochow, D.T. Hurd and R.N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley, New York, 1957.
[12] J. Boersma, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 2, p. 823, 1982.
[13] *Jikken Kagaku Kouza 18*, 4th ed., *Yuki Kinzoku Sakutai*, Japan Chem. Soc. ed., Maruzen, Tokyo, p. 470, 1991.
N.I. Sheverdina and K.A. Kocheschkov, *Methods of Elementoorganic Chemistry (Houben-Weyl)* XII/2a, Thieme Verlag 1973.
[14] R.D. Rieke, *Acc. Res. Chem.*, **10** (1977) 301.
[15] L. Zhu, R.M. Wehmeyer and R.D. Rieke, *J. Org. Chem.*, **56** (1991) 1445.
[16] E. Erdik, *Tetrahedron*, **43** (1987) 2203.
[17] N. Ishikawa and T. Kitazume, *Yuki Gosei Kagaku Kyokaishi*, **41** (1983) 432.
[18] K.-H. Thiele, E. Langguth and G.E. Müller, *Z. Anorg. Allg. Chem.*, **462** (1980) 152.
[19] P. Sartori and M. Weidenbruch, *Chem. Ber.*, **100** (1967) 3016.
[20] J. Lorberth, *J. Organomet. Chem.*, **19** (1969) 189.
[21] S.E. Denmark, J.P. Edwards and S.R. Wilson, *J. Am. Chem. Soc.*, **114** (1992) 2592.
[22] P. O'Brien, M.B. Hursthouse, M. Motevalli, J.R. Walsh and A.C. Jones, *J. Organomet. Chem.*, **449** (1993) 1.
[23] M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W.J.J. Smeets and A.L. Speck, *J. Am. Chem. Soc.*, **113** (1991) 5606.
[24] J. Dekker, J. Boersma, L. Fernholt, A. Haaland and A.L. Spek, *Organometallics*, **6** (1987) 1202.
[25] J. Dekker, J.W. Münninghoff, J. Boersma and A.L. Spek, *Organometallics*, **6** (1987) 1236.
[26] H. Schmidbaur and G. Jonas, *Angew. Chem.*, **79** (1967) 413.
[27] H.-O. Fröhlich, B. Kosan, B. Müller and W. Hiller, *J. Organomet. Chem.*, **441** (1992) 177.
[28] K. Soal and S. Niwa, *Chem. Rev.*, **92** (1992) 833.
[29] M. Westerhausen, B. Rademacher, W. Schwarz, J. Weidlein and S. Henkel, *J. Organomet. Chem.*, **469** (1994) 135.
[30] G.E.Coates and D. Ridley, *J. Chem. Soc.*, (1965)1870.
[31] J.G. Noltes and J. Boersma, *J. Organomet. Chem.*, **16** (1969) 345.
[32] J. Boersma and J.G. Noltes, *J. Organomet. Chem.*, **17** (1969) 1.
[33] M.L. Ziegler and J. Weiss, *Angew. Chem.*, **82** (1970) 931.
[34] M. Ishimori, T. Hagiwara, T. Tsuruta, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Japan*, **49** (1976) 1165.
[35] *Jikken Kagaku Kouza 25*, 4th ed., *Yuki Gosei VII, Yuki Kinzoku Shiyaku niyoru Gousei*, Japan Chem. Soc. Ed., Maruzen, Tokyo, p. 73, 1991.
[36] I. Yamamoto ed., *Yuki Kinzoku Kagoubutsu, Goseiho oyobi Riyouhou*, Tokyo Kagaku Dojin, Tokyo, p. 71. 1991.
[37] J. Furukawa and N. Kawabata, *Adv. Organomet. Chem.*, **12** (1974) 83.
[38] N. Oguni, *Kagaku Sosetsu*, **19** (1993) 143.
Noyori and M. Kitamura, *Angew. Chem. Int. Ed. Engl.*, **30** (1991) 49.
[39] J.F. Ruppert and J.D. White, *J. Org. Chem.*, **41** (1976) 550.
[40] P. Knochel and R.D. Singer, *Chem. Rev.*, **93** (1993) 2117.
[41] E. Erdik, *Tetrahedron*, **48** (1992) 9577.
[42] Y. Tamara, H. Ochiai, T. Nakamura, K. Tsubaki and Z. Yoshida, *Tetrahedron Lett.*, (1985)559.

[43] K. Soai, T. Hayasaka and S. Ugajin, *J. Chem. Soc. Chem. Commun.*, (1989) 516.

[44] Y. Tamara, H. Ochiai, T. Nakamura and Z. Yoshida, *Tetrahedron Lett.*, (1986) 955.

[45] G. Kanai, N. Miyaura and A. Suzuki, *Chem. Lett.*, (1993)845.

[46] R. Rossi, A. Carpita, F. Bellina and P. Cossi, *J. Organomet. Chem.*, **451** (1993) 33.

[47] K.A. Agrios and M. Srebnik, *J. Organomet. Chem.*, **444** (1993) 15.

[48] J. Boersma, F.J.A. Des Tombe, F. Weijers and G.J.M. van der Kerk, *J. Organomet. Chem.*, **124** (1977) 229.

[49] K.-H. Thiele and J. Köhler, *J. Organomet. Chem.*, **12** (1968) 225.

[50] S. Moorhouse and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, (1974) 2187.

[51] A. Lachowicz and K.-H. Thiele, *Z. Anorg. Allg. Chem.*, **431** (1977) 88.

[52] M. Taniguchi, K. Oshima and K. Utimoto, *Chem. Lett.*, (1992)2135.

[53] C.E. Tucker, B. Greve, W. Klein and P. Knochel, *Organometallics*, **13** (1994) 94.

[54] R. Noyori, S. Suga, K. Kawai, S. Okada, M. Kitamura, N. Oguni, M. Hayashi, T. Kaneko and Y. Matsuda, *J. Organomet. Chem.*, **382** (1990) 19.

[55] M. Asami and S. Inoue, *Chem. Lett.*, (1991)685.

[56] W. Brieden, R. Ostwald and P. Knochel, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 582.

[57] K. Soai, S. Yokoyama, K. Ebihara and T. Hayasaka, *J. Chem. Soc. Chem. Commun.*, (1987)1690.

[58] M. Kitamura, S. Suga, K. Kawai and R. Noyori, *J. Am. Chem. Soc.*, **108** (1986) 6071.

[59] K. Tanaka, *Yuki Goesei Kagaku Kyokaishi*, **51** (1993) 620.
K. Tanaka, H. Ushio and H. Suzuki, *J. Chem. Soc. Chem. Commun.*, (1989) 1700.

[60] K. Soai and T. Hayase, *Yuki Goesei Kagaku Kyokaishi*, **53** (1995) 138.
R. Noyori and M. Kitamura, *Angew. Chem. Int. Ed. Engl.*, **30** (1991) 49.
K. Soai and S. Niwa, *Chem. Rev.*, **92** (1992) 833.

[61] C.E. Tucker and P. Knochel, *J. Am. Chem. Soc.*, **113** (1991) 9888.

[61a] C. Elschenbroich and A. Salzer, *Organometallics*, VCH, Weinheim, p. 48, 1989.

[62] E. Nakamura, S. Akoi, K. Sekiya, H. Oshino and I. Kuwajima, *J. Am. Chem. Soc.*, **109** (1987) 8056.

[63] E. Nakamura, *Yuki Goesei Kagaku Kyokaishi*, **47** (1989) 931.

[64] N.L. Drake, C.M. Eaker and W. Shenk, *J. Am. Chem. Soc.*, **70** (1948) 677.

[65] M. Harfenist and E. Magnien, *J. Am. Chem. Soc.*, **78** (1956) 1060.

[66] A. Balsamo, P.L. Barili, P. Crotti, M. Ferretti, B. Macchia and F. Macchia, *Tetrahedron Lett.*, (1974)1005.

[67] M.S. Newman and F.J. Evans, Jr., *J. Am. Chem. Soc.*, **77** (1955) 946.

[68] R.L. Shriner, *Organic Reactions*, **1** (1944) 1.

[69] M.W. Rathke, *Organic Reactions*, **22** (1975) 423.

[70] H.B. Henbest, E.R.H. Hones and I.M.S. Walls, *J. Chem. Soc.*, (1949)2696.

[71] M. Bellassoued, R. Couffignal and M. Gaudemar, *J. Organomet. Chem.*, **36** (1972) C33.

[72] D.A. Cornforth, A.E. Opara and G. Read, *J. Chem. Soc. (C)*, (1969) 2799.

[73] J.F. Fauvarque and A. Jutand, *J. Organomet. Chem.*, **132** (1977) C17.

[74] F. Orsini and F. Pelizzoni, *Syn. Commun.*, **17** (1987) 1389.

[75] C.E. Tucker, T.N. Majid and P. Knochel, *J. Am. Chem. Soc.*, **114** (1992) 3983.

[76] D.A. Shirley, *Organic Reactions*, **8** (1954) 28.

[76a] R.G. Jones, *J. Am. Chem. Soc.*, **69** (1947) 2350.

[77] M. Arai, T. Kawasuji and E. Nakamura, *Chem. Lett.*, (1993)357.

[78] Y. Tamaru, H. Ochiai, T. Nakamura and Z. Yoshida, *Tetrahedron. Lett.*, (1986) 955.

[79] H.E. Simmons, T.L. Cairns and S.A. Vladuchick, *Organic Reactions*, **20** (1973) 1.

[80] G. Wittig and K. Schwarzenbach, *Liebigs Ann. Chem.*, **650** (1961) 1.

[81] R.D. Smith and H.W. Simmons, *Organic Synthesis*, **41** (1961) 72.

[82] R.S. Shank and H. Shechter, *J. Org. Chem.*, **24** (1959) 1825.

[83] H.E. Simmons and R.D. Smith, *J. Am. Chem. Soc.*, **81** (1959) 4256.

[84] S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83** (1961) 3235.
[85] E.P. Blanchard and H.E. Simmons, *J. Am. Chem. Soc.*, **86** (1964) 1337.
[86] E. LeGoff, *J. Org. Chem.*, **29** (1964) 2048.
[87] S. Sawada and Y. Inouye, *Bull. Chem. Soc. Japan*, **42** (1969) 2669.
[88] J.A. Staroscik and B. Rickborn, *J. Org. Chem.*, **37** (1972) 738.
[89] S. Miyano and H. Hashimoto, *Bull. Chem. Soc. Japan*, **47** (1974) 1500.
[90] N. Kawabata, T. Nakagawa, T. Nakao and S. Yamashita, *J. Org. Chem.*, **42** (1977) 3031.
[91] K.J. Klabunde and T.O. Murdock, *J. Org. Chem.*, **44** (1979) 3901.
[92] A.B. Charette, B. Côté and J.-F. Marcoux, *J. Am. Chem. Soc.*, **113** (1991) 8166.
[93] H.E. Simmons and R.D. Smith, *J. Am. Chem. Soc.*, **80** (1958) 5323.
[94] N.A.D. Varey and H.C. Clark, *Can. J. Chem.*, **46** (1968) 649.
[95] G. Sonsnovsky and J.H. Brown, *Chem. Rev.*, **66** (1966) 529.
[96] S. Inoue, K. Izui and K. Tanaka, *Genai Kagaku Zokan*, **25** (1994) 90.
[97] S. Inoue, H. Koinuma and T. Tsuruta, *Polymer Lett.*, **7** (1969) 287.
[98] S. Inoue, H. Koinuma and T. Tsuruta, *Makromol. Chem.*, **130** (1969) 210.
[99] S. Inoue, *Chemtech*, September (1976) 588.
[100] T. Hirano and S. Inoue, *Yuki Goesei Kagaku Kyokaishi*, **34** (1976) 333.
S. Inoue, H. Koinuma and T. Tsuruta, *Polymer Lett.*, **7** (1969) 287.
S. Inoue, H. Koinuma and T. Tsuruta, *Makromol. Chem.*, **130** (1969) 210.
[101] M. Nakano, *Yuki Goesei Kagaku Kyokaishi*, **42** (1984) 665.

6 Organoboron Compounds

6.1 INTRODUCTION

Speaking of organoboron compounds, the hydroboration reaction found by H. C. Brown is well known. H. C. Brown started to study organoboron compounds in the 1930s, more than 50 years ago. He found the hydroboration reaction in 1959, and was awarded the Nobel prize in 1979. [1]. Even though he is now more than 80 years old, he has still been studying the subject energetically. He says he has published 30 articles per year before reaching retirement age as the faculty, and after his retirement by age, his publications have increased to 40 articles per year, and furthermore many better articles have resulted. [1].

H.J. Hildebrand, who studied until he was more than 100 years old, was a chemist from the United States, and his work was reviewed in *Kagaku to Kogyo*, the Japanese chemical journal, in 1984 [2]. H. C. Brown and J. H. Hilderbrand are good examples that we are able to continue doing excellent research even if we become 70 or 80 years old, if we make the effort. They tell us that we younger people should not complain 'we are already 60 or 70 years old'.

The characteristic reactions of the organoboron compounds are not only hydroboration but also highly stereospecific reactions.

This chapter shows mainly the characteristics of these organoboron compounds.

6.2 BORON

Borite ($Na_2B_4O_7 \cdot 10H_2O$) and kernite ($Na_2B_4O_9 \cdot 4H_2O$) are mainly used as ores for boron. These ores are leached with warm water to form the borate salt. Hydrochloric acid is added to the salt and boric acid (H_3BO_3) is crystallized. The boric acid is heated at 1000 °C to give the anhydride oxide (B_2O_3). Magnesium or aluminum metal is added to the oxide, and heated at 900–1000 °C to give 90–92 % purity boron [3–8]. Electrolysis is carried out on B_2O_3–KCl–KBF_4 or KCl–KBF_4 as the electrolyte, using graphite as the anode and iron as the cathode in a graphite crucible electrolytic cell at 600–1000 °C, to yield 95–98 % purity boron on the cathode [8].

$$Na_2B_4O_7 \xrightarrow{H^+} H_3BO_3 \xrightarrow{1000^\circ C} B_2O_3 \xrightarrow[\text{reduction}]{\text{Mg or Al, 900-1000}^\circ\text{C}} B \quad (6.1)$$

Boron of 99 % or more purity is produced by passing boron trichloride (BCl_3) with hydrogen through a metal filament such as tungsten, tantalum or titanium at 1000 °C or higher temperature. With BBr_3 in the place of BCl_3, boron of 99.9 % or more purity is prepared [8].

Boron is the thirteenth element in the periodic table and it is in the same group as aluminum. However, it is more chemically similar to silicon. The physical and chemical properties of boron are shown in Table 6.1 [3–7]. Boron is a lustrous gray-black colored and the second hardest element, with the diamond allotrope of carbon being the hardest. In the crystal, the β-rhombohedral form is thermodynamically stable, and the amorphous boron becomes the β-rhombohedral form by heating at 1200 °C. At 1500 °C or more, it becomes the α-rhombohedral [4].

The atomic radius of boron is small and its covalent property is high since the ionization potentials are high. Therefore, the simple substance or its compound has a tendency to form a very complicated and diverse structure. The outer electronic configuration is $2s^22p^1$ and predominately trivalent. However, simple B^{3+} ions do

Table 6.1 Physical and chemical properties of boron [3–7]

Property	Value
mp, °C	2190
bp, °C	3660
crystal structure	amorphous, β-rhombohedral, α-rhombohedral, four tetragonal
density, 20 °C, g/cm^3	
β-rhombohedral	2.35
α-rhombohedral	2.46
hardness	
Knoop, HK	2110–2580
Mohs, modified scale	11 (diamond = 15)
electrical resitivity; 300 °K, Ω cm	
amorphous	7.5×10^2
β-rhombohedral	10^6–10^7
coefficient of thermal expansion per °C	
from 25 to 1050 °C	5–7×10^6
filamentary boron	
tensile strength, Mpa(psi)	3450–4830 (500 000–700 000)
Young's modulus, Mpa(psi)	3040–3330 (440 000–480 000)
ionization energy, kj/mol (eV)	
$B \rightarrow B^+$	798 (8.27)
$B \rightarrow B^{2+}$	2426 (25.15)
$B^{2+} \rightarrow B^{3+}$	3658 (37.92)
electron affinity	32 KJ/mol (0.332 eV)
electronegativity	2.01 (Mulliken)
ionic radius	0.025 nm
atomic radium	0.080–0.095 nm

not exist. Boron is an electron-pair acceptor, i.e., a Lewis acid since boron has more orbitals available for bonding than electrons, and boron has a tendency to form multi-center bonds. Other dominant characteristics are the high affinity for oxygen and tendency to combine with most metals [4].

Boron is relatively resistant to chemical attack at room temperatures. For example, chlorine does not react at room temperatures. However, the reaction starts at 500 °C. Reaction with oxygen starts at about 600 °C but is restrained by the formation of a glassy liquid film (B_2O_3) on the surface of boron particles [4].

Boron acts as an effective reducing agent. For example, water vapor is reduced at 800 °C to give H_2 and B_2O_3.

Boron does not react with acids or bases such as hydrochloric acid or aqueous NaOH. However, vigorous reaction occurs with oxidizing concentrated nitric acid [4].

6.3 PREPARATION OF ORGANOBORON COMPOUNDS

Organoboron compounds are mainly prepared by transmetalation (alkylation) and hydroboration [4,9–20]. The transmetalation is the reaction of Grignard reagents (eq. (6.2)), organoaluminum compounds (eq. (6.3)), organotin compounds, organozinc compounds or organoalkali metal compounds with boron halides or boron esters, etc. In particular, the organoaluminum compounds are available as the most cheap raw materials. The reaction is an exothermic reaction. It requires that the temperature is kept below 100 °C, and the product is easily isolated by distillation [4].

$$3\,RMgX + BF_3 \xrightarrow{Et_2O} R_3B + 3\,MgXF \qquad (6.2)$$

$$R_3Al + B(OR)_3 \longrightarrow R_3B + Al(OR)_3 \qquad (6.3)$$

In the transmetalation, as the difference in electronegativity of the metals increases, the faster the reaction proceeds. The order of the reactivity is as follows:

$$K > Na > Li > Mg > Al > Zn > Cd > Sn$$

On the other hand, the order of the reactivity of exchange reaction on the substituents bonded with boron is as follows:

$$X \geqslant OR > SR > NH$$

It is difficult to synthesize a simple mono-substituted product (RBX_2) or di-substituted product (R_2BX) selectively since the reaction is stepwise [9].

The reaction in which a metal hydride is added to olefins or acetylenes is called a hydrometalation. The metals used in the hydrometalation reactions are B, Al, Si, Ge, Sn, Zr, Cu, Fe, Co, etc. Of these reactions, the hydrometalation of boron, that is, hydroboration is the most well known. Diborane is the basic raw material for the hydroborations, and it is prepared by many methods. For example, as shown in eq. (6.4), diborane is prepared by the reaction of $NaBH_4$ with $BF_3 \cdot OEt_2$ in glyme ($MeOCH_2CH_2OMe$).

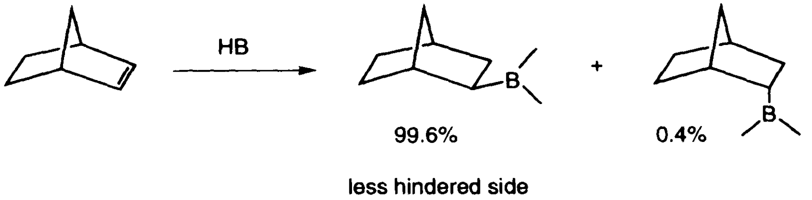
$$3NaBH_4 \quad + \quad 4BF_3 \cdot OEt_2 \longrightarrow 2B_2H_6 \quad + \quad 3NaBF_4 \qquad (6.4)$$

Diborane is available as the complex of THF ($BH_3 \cdot THF$) by dissolving it in THF for easier handling. In the reaction with olefins (eq. (6.5)) or acetylenes, generally, trialkylborane is produced by the addition reaction of three hydrides.

$$3RCH{=}CH_2 \quad + \quad \tfrac{1}{2}B_2H_6 \longrightarrow (RCH_2CH_2)_3B \qquad (6.5)$$

The representative hydroboration reagents are shown in Figure 6.1 [9–12,21–27]. Hydroborations have the following six characteristics [9,10,21].

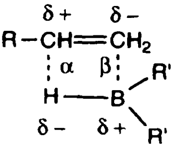
(1) The addition takes place predominantly from the less hindered side of the double bond. A mono-substituted product (RBH_2) or disubstituted product (R_2BH) is able to be synthesized selectively when a boron atom is bonded with a large bulky alkyl group, since the bond length of B–C (1.56 Å in Me_3B [5]) is short (for example, the synthesis of $IPCBH_2$ or IPC_2BH as shown in Figure 6.1). Highly stereoselective reactions proceed since the reactions take place at the less hindered side as shown in eq. (6.6).



(6.6)

(2) *Anti-Markovnikov addition.* As shown in eq. (6.7), anti-Markovnikov addition in hydroboration proceeds because of the synergistic effect of a steric effect by mutual repulsions of bulky substituents R and R′, and an electrostatic effect of

$$R\text{-}CH{=}CH_2 \quad + \quad HBR'_2 \longrightarrow R\text{-}CH_2CH_2BR'_2 \xrightarrow{[O]} R\text{-}CH_2CH_2\text{-}OH$$



(6.7)

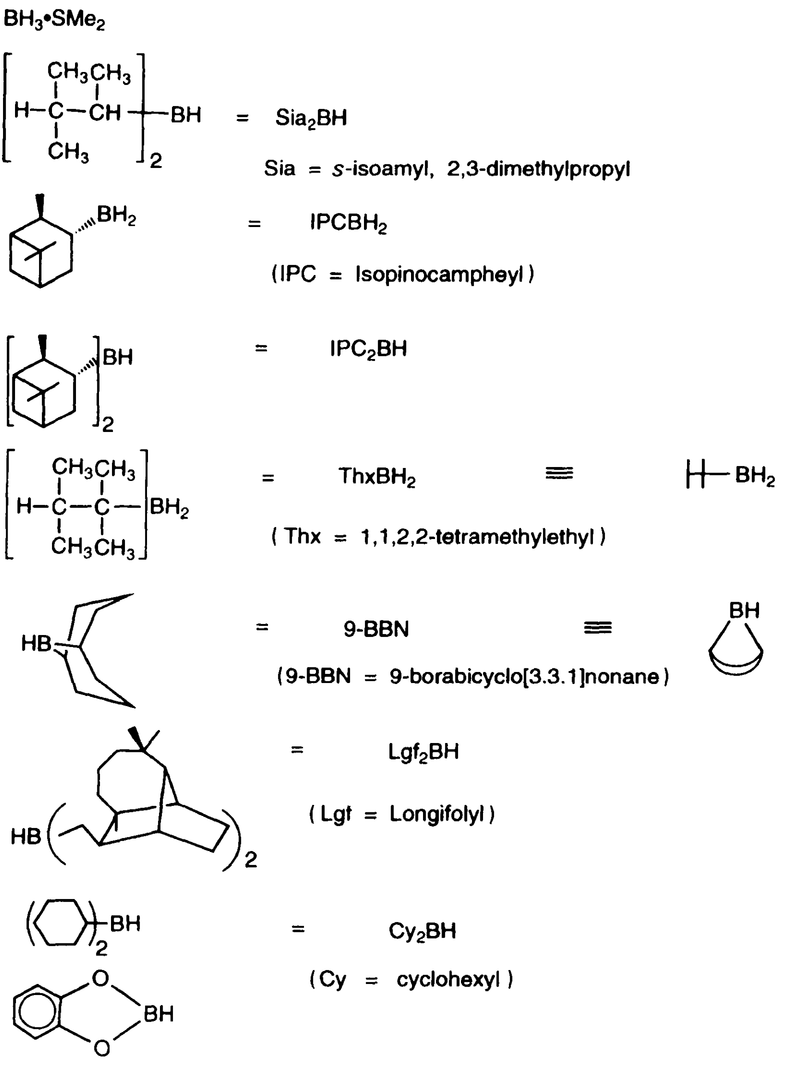
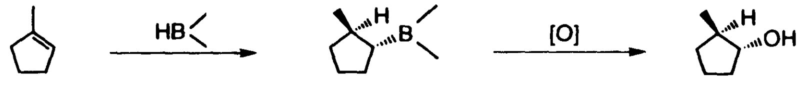


Figure 6.1 Representative reagents for hydroboration [9–12,21–27].

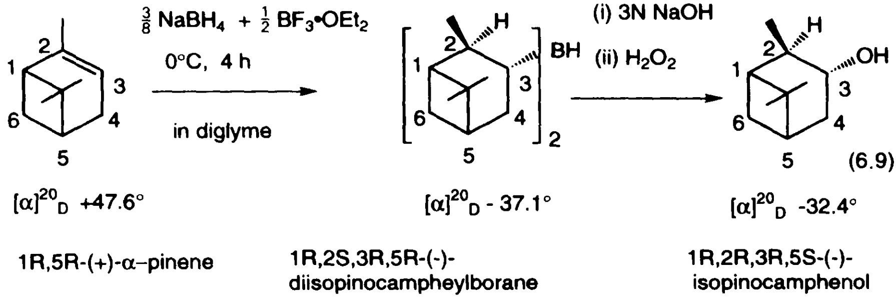
olefins and boron hydrides. In the polarization of olefins when electron-donating groups such as alkyl are bonded, the electron density of the carbon at the β-position becomes higher by an inductive effect (I effect) and by a resonance effect (R effect). Hence, the Markovnikov reaction proceeds when the R is bonded with an electron-withdrawing group [9–11].

(3) *cis-addition.* As shown in eq. (6.8), in hydroboration, *cis* addition proceed stereoselectively without exception. It is easily understandable by considering the four center transition state as shown in eq. (6.7) [9].

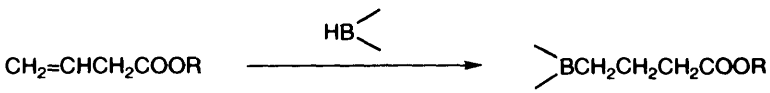


(6.8)

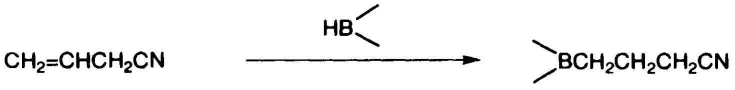
(4) *Rearrangements are not involved.* Hydroboration is suitable for asymmetric syntheses since no rearrangement of the carbon skeleton have been observed. If we use different stereospecific raw materials to the reaction shown in eq. (6.9), the products are also the different stereospecific isomers. Namely, with various stereospecific raw materials, we easily prepared the corresponding stereospecific products. For example, using raw materials (-)-α-pinenes having an opposite angle of rotation to the reaction shown in eq. (6.9), the product is 1R, 2R, 3R, 5R-(-)-isopinocamphenol [11,27a].



(5) *Most functional groups can tolerate hydroboration.* As shown in eqs. (6.10) and (6.11), even if olefins have functional groups such as alkoxycarbonyl group and cyano group, the addition reactions to a double bond proceed [9,14].



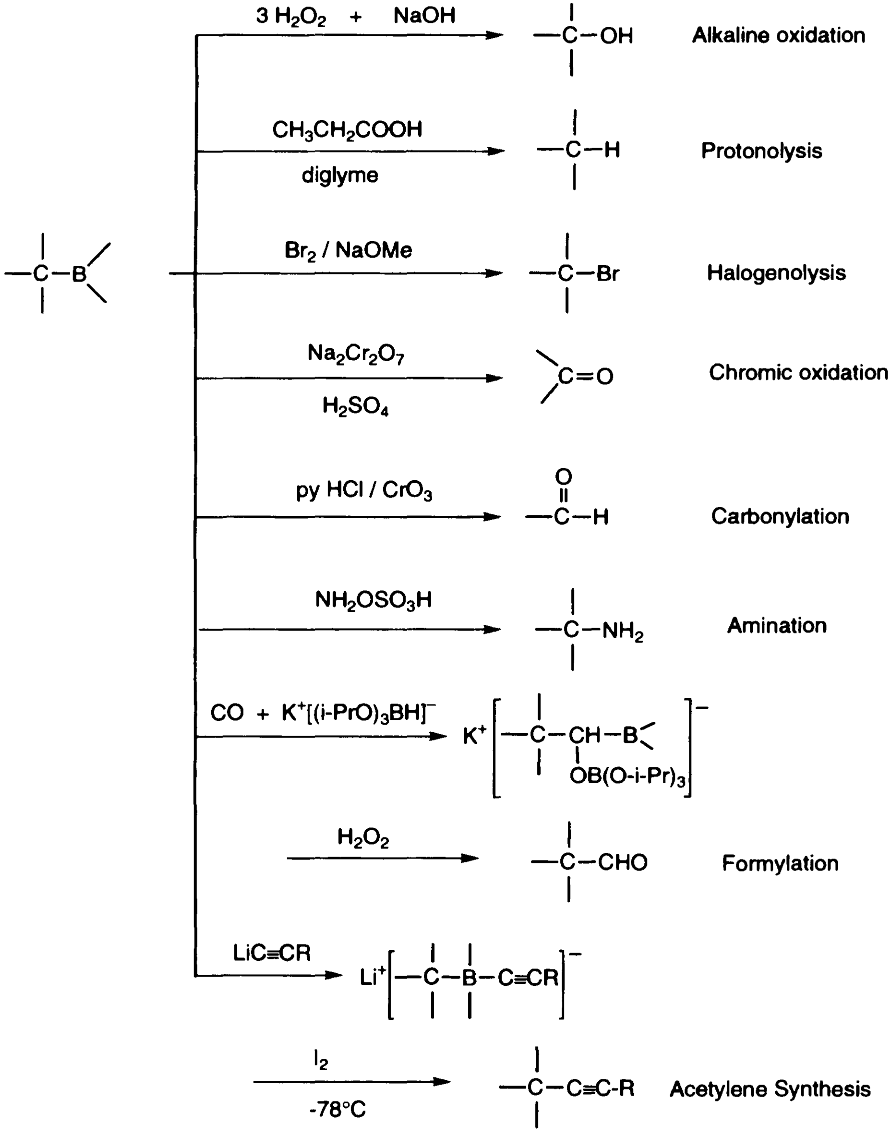
$$CH_2{=}CHCH_2COOR \xrightarrow{HB<} {>}BCH_2CH_2CH_2COOR \qquad (6.10)$$



$$CH_2{=}CHCH_2CN \xrightarrow{HB<} {>}BCH_2CH_2CH_2CN \qquad (6.11)$$

(6) *Reactions are essentially instantaneous and quantitative.* The hydrometalation with many metal compounds usually shows both items (5) and (6) of the above. For hydroboration, the first four items are the major distinctive characteristics.

Organoboron compounds obtained by hydroboration are converted to the various kinds of organoboron compounds as shown in Scheme 6.1 [10,16,28–33].



Scheme 6.1 [10,16,28–33]

6.4 CHARACTERISTICS OF ORGANOBORON COMPOUNDS

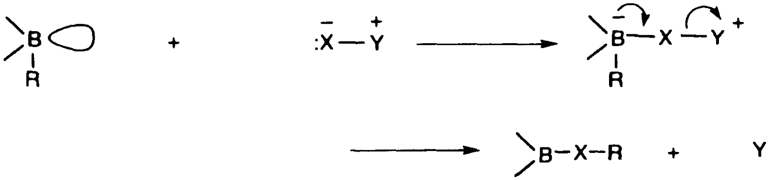
Organoboron compounds shown distinctive reactions caused by their three characteristics [9,15].

(1) A vacant p orbital
(2) Small atomic radius (0.025 nm) and small relative atomic mass (10.811)
(3) Relatively large electronegativity (2.0) as a metal

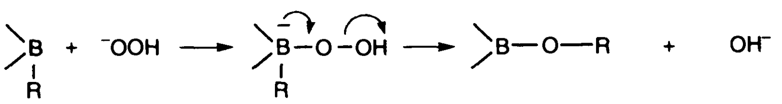
Organoboron compounds tend to be stabilized by a pπ–pπ conjugation with a lone pair of electrons and an anion for the adjacent atom since boron has vacant p orbitals, and reaction via radical anions is liable to proceed. Boron bonds with many anionic species such as a carboanion and an alkoxyanion to give the ate complex. If the anionic species has a group which is liable to be eliminated, the reaction does not stop at the step of the ate complexes as shown in eq. (6.12). The

$$R_3B \quad + \quad R'M \longrightarrow M^+[R_3B\text{-}R']^- \quad (6.12)$$

reaction gives the thermally stable compounds by 1,2-rearrangement as shown in eq. (6.13) [9]. For example, in the oxidation of boron with alkaline hydroperoxide, the hydroperoxide anion ($^-$OOH) attacks nucleophilically, and then the 1,2-rearrangement of R and elimination of hydroxy anion (OH$^-$) at the same time forms an ether, and its hydrolysis yields the alcohol and hydroxy diborane [9]. Boron acts to stabilize the radicals of the adjacent atom by the pπ–pπ conjugation. Therefore, in a radical halogenation with alkylboran, hydrogen abstraction proceeds at the α-position, and proceeds with halogenation at the same position as shown in Scheme 6.2 [9]. In this reaction in the presence of water the OH$^-$ attacks nucleophilically to the boron, and the alkyl group gives rise to the 1,2-rearrangement similar to the reactions shown in eqs. (6.13) and (6.14). In the presence of bromine, boron further reacts with the α-carbon bonded with the more alkyl groups, and yield monoalkylboron by the 1,2-rearrangement. Further, the oxidation gives a tertiary alcohol [9].

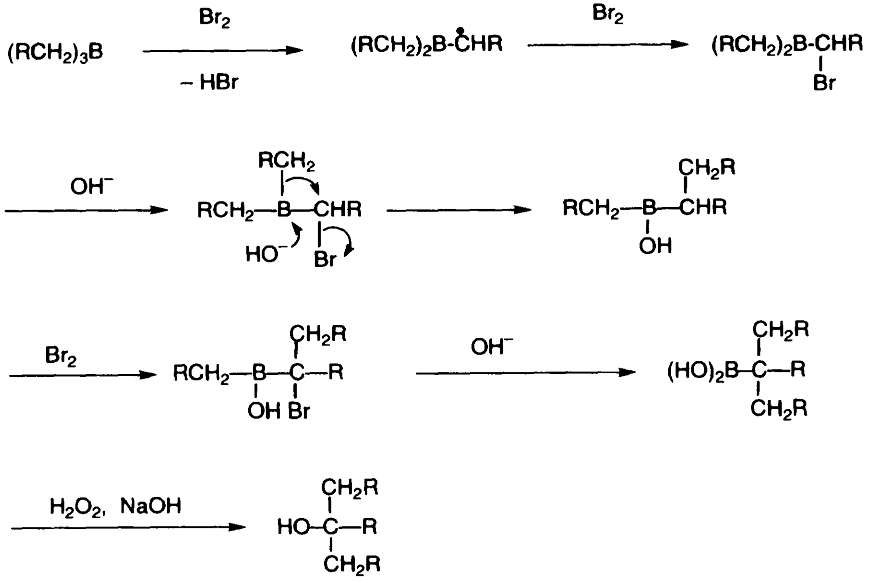


(6.13)

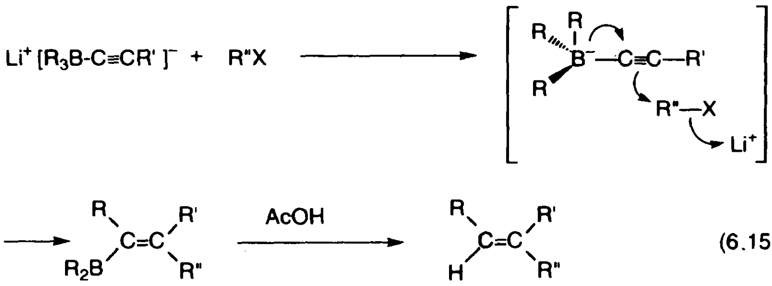


(6.14)

In the ate complex of boron, the nucleophilic reaction with electrophiles tends to proceed. For example, the reaction is useful for synthetic reactions of olefins having three substituents as shown in eq. (6.15) [9].



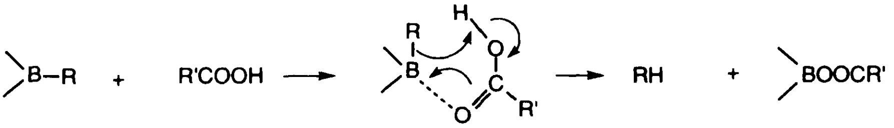
Scheme 6.2 [9]



(6.15)

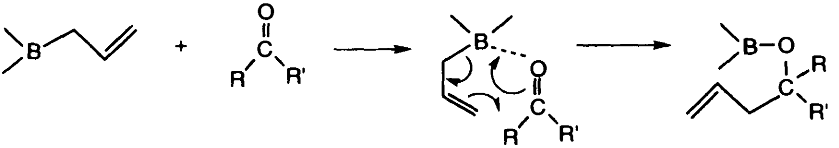
R" = CH_2=$CHCH_2$, R'''$COCH_2$

Organoboron compounds are stable in water, alcohols and inorganic acids. However, they easily react with carboxylic acids and are decomposed. This reaction is considered to be due to the boron atom being liable to be attacked by a carbonyl anion, and the concerted reaction via a six-membered ring transition state proceeds as shown in eq. (6.16) [9].



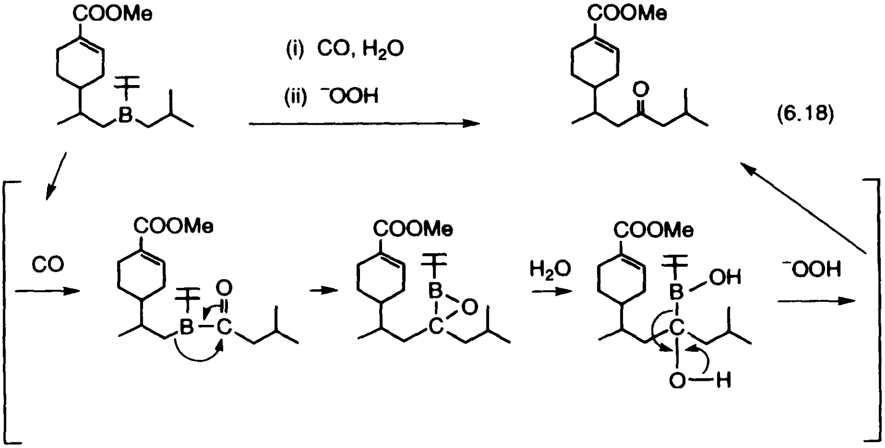
(6.16)

Allylboron, the allyl addition to carbonyl compound, is liable to easily proceed as shown in eq. (6.17). This reaction is also considered via the six-membered ring transition state similar to the reactions shown in eq. (6.16) [9].



(6.17)

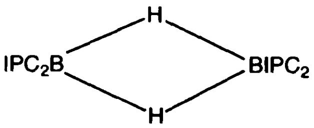
Organoboron compounds react with carbon monoxide, which is the simplest carbonyl compound, under conditions of high temperature and pressure. Many reactions with transition metal compounds such as Fe, Ni and Co compounds are known. However, few carbonylations with main group metal compounds proceed. These reactions can be applied to, for example, the carbonylation shown in eq. (6.18) [9,34,35].



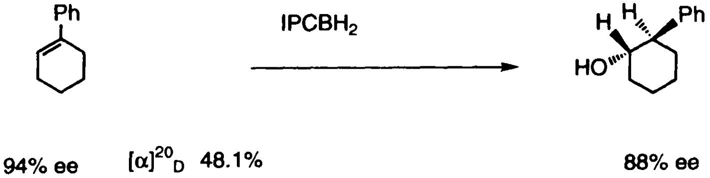
(6.18)

Hydroboration and asymmetric reductions proceed with high stereoselectivity because of the small atom radius and the large electronegativity of boron [22]. Hence, organoboron compounds are used for asymmetric reactions, especially for asymmetric reduction [9,22,36]. Both the yield and the optical yield of asymmetric reactions with organoboron compounds are high, and the isolation of chiral products is easy. Therefore, these reactions are exploited for syntheses of terpenes [22].

Enzyme reactions are the highest stereoselectivity reactions. The reaction of organoboron compounds also achieves very high stereoselectivities, similar to those from enzyme reactions. As reagents for asymmetric syntheses IPC_2BH, $IPCBH_2$ and Lgf_2BH, etc., are shown in Figure 6.1 [22]. IPC_2BH is widely used in laboratories as an asymmetric synthetic reagent for alcohols, halides, amines, ketones, hydrocarbons and α-amino acids, etc. These reagents are synthesized by the reaction shown in eq. (6.9). As described in the previous section, the chirally different IPC_2BH is prepared from the raw material of the corresponding chiral. The IPC_2BH forms dimer with the hydrogen bridged structure.

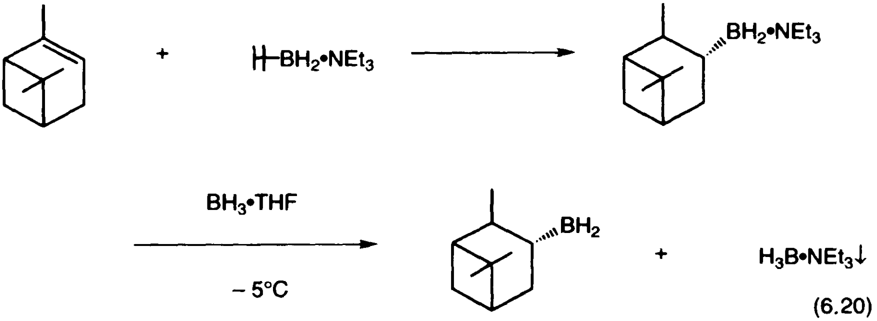


In the reaction shown in eq. (6.9), if the reaction proceeds with 15 % excess of 95 % ee α-pine at 0 °C for 3 d, the small amount of chiral isomer is concentrated in the solution and 99.8 % ee IPC_2BH is obtained. It is oxidized to give a highly chiral alcohol [22]. The reactivity of IPC_2BH to bulky olefins is low; then the optical purity of the product is low. However, $IPCBH_2$ is reactive, for example 88 % ee alcohol is obtained as shown in eq. (6.19) [22].



(6.19)

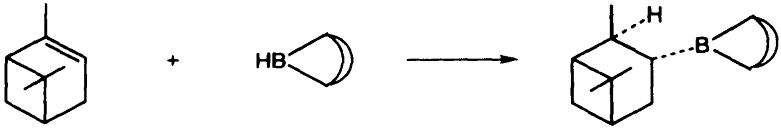
α-Pinene reacts with a bulky $ThBH_2{\cdot}NEt_2$ to give an organoboron amine salt, and then the amine salt is reacted with $BH_3{\cdot}THF$ to give $IPCBH_2$ by separating amine moiety as the boron amine salt as shown in eq. (6.20) [22].



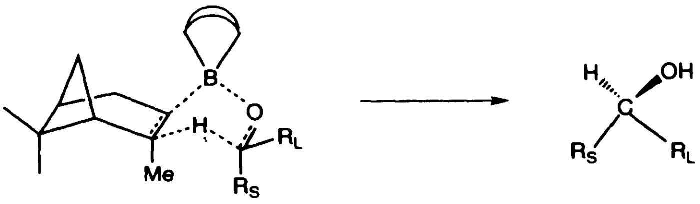
(6.20)

Lgf_2BH (see Figure 6.1) is suitable for the reaction in which the intermediate bulkiness between IPC_2BH and $IPCBH_2$ is required [22].

α-Pinene reacts with 9-BBN (see Figure 6.1) [37] to give a chiral trialkylboron as shown in eq. (6.21). This chiral trialkylboron is able to perform a reduction by

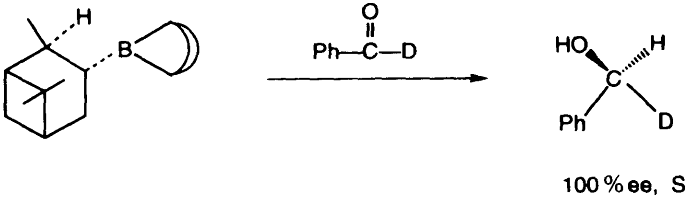


(6.21)



Scheme 6.3 Proposed transition state made for asymmetric reduction with B-isopinocamphenyl-9-borabicyclo[3.3.1]nonane [36,40].

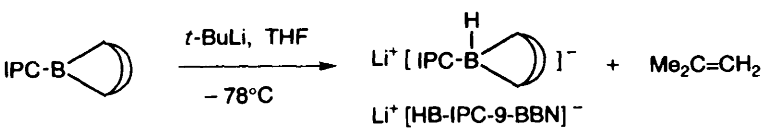
the hydrogen at the β-position (see Scheme 6.3), and it is used for the reduction of various kinds of compounds having a functional group. For example, it reacts with deuterated benzaldehyde to give the benzylalcohol of 100 % ee as shown in eq. (6.22) [22,38,39]. The reaction of the trialkylboron is considered to proceed via a



(6.22)

four center mechanism as shown in Scheme 6.3 [22,36,40]. Halide (IPC_2BCl) (eq. 6.23)) and the ate complex (eq. (6.24)), etc., are used as the asymmetric reducing agents [22]. The halide (IPC_2BCl) is able to give various kinds of 90–100 ee carbonyl compounds and it is used as the highly stereoselective reducing agent. The reaction mechanism of the halide is considered to be the same as the four center mechanism shown in Scheme 6.3 [36,40]. The ate complex, for example, gives the 3–37 % ee product in reductions of various kinds of ketones [40a]. As we have seen, highly stereoselective reactions are able to proceed when we select the appropriate organoboron compounds.

$$\mathrm{IPC_2BH} \xrightarrow{\mathrm{HCl}} \mathrm{IPC_2BCl} \qquad (6.23)$$

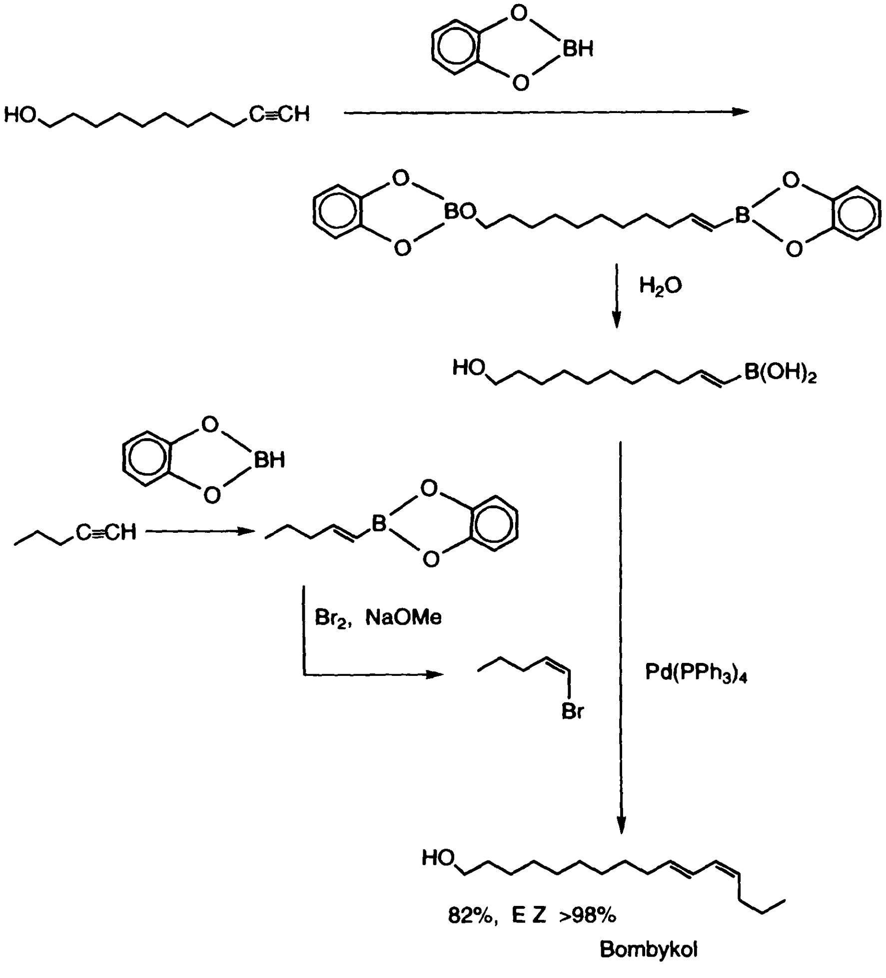


(6.24)

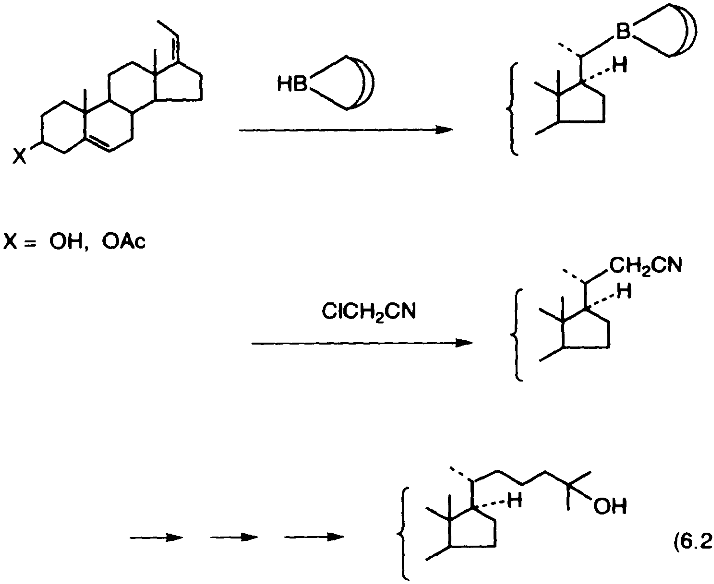
6.5 APPLICATIONS OF ORGANOBORON COMPOUNDS

The organoboron compounds have many characteristics as described in the previous section and they are utilized for syntheses of pharmaceuticals and perfumes [28]. For example, they are used for the production of ecdysone, which is a hormone for ecdyses and pupation of insects, and for the steroids having the same branched chain as metabolic product of viamine D.

As shown in eq. (6.25), hydroboration of Z-17(20)-ethylidenesteroid with 9-BBN gives the desired same stereoconformation 20R product, followed by the substitution of $ClCH_2CN$, and reduction with organoaluminum compounds, etc. to give 20R-25-hydroxycholesterol in high yields [41–43].



Scheme 6.4 Stereospecific synthesis of pheromone bombykol [44–47].



(6.25)

Bombykol is an estrogenic hormone ((10E,12Z)-hexadecadiene-1-ol) which induces sexual excitement in a male silkworm. Bombykol is prepared by the hydroboration of acetylene compounds with a catecol boron compound and a cross coupling reaction with palladium catalyst, etc., as shown in Scheme 6.4 [41–47]. The organoboron compounds are used for leucotriene intermediates [48], L-ribose and amino acids [47], etc., as the others.

Recently haloboration reactions [49,50], boron polymers [51,52], phosphine-boron [53] and syntheses of intramolecularly coordinated five-membered ring compounds [54–60], etc., have been reported.

REFERENCES

[1] H.C. Brown, (translator: A. Suzuki), *Kagaku to Kogyo*, **42** (1989) 90.

[2] K. Shinoda, *Kagaku to Kogyo*, **37** (1984) 257.

[3] Kirk-Othmer, *Encylopedia of Chemical Technology*, 3rd. ed. John Wiley, New York, vol.4, p.62, 1980.

[4] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol. A4, p.281, 1990.

[5] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, p.1215, 1987.

[6] *Kagaku Daijiten*, Tokyo Kagaku Dojin, p. 2215, 1989.

[7] *11892 no Kagaku Shohin*, Kagaku Kogyo Nipposha, p. 144, 1992.

[8] *Kagaku Binran Ooyohen*, Japan Chemical Society, Maruzen, Tokyo, p. 301, 1980.

[9] Y. Yamamoto and Y. Naruta, *Yuki Kizoku Kagaku*, Maruzen, Tokyo, p. 39, 1983.

[10] H.C. Brown, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7, p. 111, 1982.

[11] M. Zaidlewicz, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7, p. 143, 1982.
[12] M. Zaidlewicz, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7, p. 161, 1982.
[13] M. Zaidlewicz, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7, p. 199, 1982.
[14] M. Zaidlewicz, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7, p. 229, 1982.
[15] E. Negishi, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7, p. 255, 1982.
[16] E. Negishi, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7,p. 265, 1982.
[17] E. Negishi, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.a. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7, p. 303, 1982.
[18] E. Negishi, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7, p. 323, 1982.
[19] E. Negishi, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7, p. 337, 1982.
[20] E. Negishi, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.7, p. 349, 1982.
[21] H.C. Brown and P.V. Ramachandran, *Pure Appl. Chem.*, **63** (1991) 307.
[22] H.C. Brown, P.K. Jadhav and A.K. Mandal, *Tetrahedron*, **37** (1981) 3547.
[23] H.C. Brown and A.W. Moerikofer, *J. Am. Chem. Soc.*, **84** (1962) 1478.
[24] P.K. Jadhav and H.C. Brown, *J. Org. Chem.*, **46** (1981) 2988.
[25] A.K. Mandal, P.K. Jadhav and H.C. Brown, *J. Org. Chem.*, **45** (1980) 3543.
[26] D.A. Evans and G.C. Fu, *J. Org. Chem.*, **55** (1990) 2280.
[27] H.C. Brown and B. Singaram, *Acc. Chem. Res.*, **21** (1988) 287.
[27a] G. Zweifel and H.C. Brown, *J. Am. Chem. Soc.*, **86** (1964) 393.
[28] M. Follet, *Chem. Ind.*, 17 Feb(1986)123.
[29] H.C. Brown and B. Singaram, *Pure Appl. Chem.*, **59** (1987) 879.
[30] H.C. Brown, J.L. Hubbard and K. Smith, *Synthesis Commun.*, (1979) 701.
[31] H.C. Brown, E.F. Knights and R.A. Coleman, *J. Am. Chem. Soc.*, **91** (1969) 2144.
[32] A. Suzuki, N. Miyaura, S. Abiko, M. Itoh, M.M. Midland, J.A. Sinclair and H.C. Brown, *J. Org. Chem.*, **51** (1986) 4507.
[33] Japan Chem. Soc. Ed., *Yuki Kagaku Jikken Koza 25, Yuki Gosei VII*, Maruzen, Tokyo, p. 83, 1991.
[34] G.M.L. Cragg, *J. Chem. Educ.*, **46** (1969) 794.
[35] H.C. Brown and E. Negishi, *J. Am. Chem. Soc.*, **89** (1967) 5285.
[36] H.C. Brown and V. Ramachandran, *Acc. Chem. Res.*, **25** (1992) 16.
[37] H.C. Brown and S.U. Kulkarni, *J. Organomet. Chem.*, **218** (1981) 299.
[38] M.M. Midland, S. Greer, A. Tramontano and S.A. Zderic, *J. Am. Chem. Soc.*, **101** (1979) 2352.
[39] M.M. Midland, A. Tramontano and S.A. Zderic, *J. Am. Chem. Soc.*, **99** (1977) 5211.
[40] H.C. Brown, J. Chandrasekharan and P.V. Ramachandran, *J. Am. Chem. Soc.*, **110** (1988) 1539.
[40a] S. Krishnamurthy, F. Vogel and H.C. Brown, *J. Org. Chem.*, **42** (1977) 2534.
[40b] H.C. Brown and P.V. Ramachandran, *Pure Appl. Chem.*, **66** (1994) 201.
[40c] K. Burgess, W.A. van der Donk, S.A. Westcott, T.B. Marder, R.T. Baker and J.C. Calabrese, *J. Am. Chem. Soc.*, **114** (1992) 9350.
[41] Y. Yamamoto and J. Yamada, *Kagaku to Seibutsu*, **24** (1985) 515.
M.M. Midland and Y.C. Kwon, *J. Org. Chem.*, **46** (1981) 229.
M.M. Midland and Y.C. Kwon, *Tetrahedron Lett.*, (1982)2077.
[42] M.M. Midland and Y.C. Kwon, *J. Org. Chem.*, **46** (1981) 229.

[43] M.M. Midland and Y.C. Kwon, *Tetrahedron Lett.*, (1982)2077.
[44] A. Suzuki, *Pure Appl. Chem.*, **57** (1985) 1749.
[45] N. Miyaura, H. Suginome and A. Suzuki, *Tetrahedron Lett.*, (1983) 1527.
[46] N. Miyaura, M. Satoh and A. Suzuki, *Tetrahedron Lett.*, (1986) 3745.
[47] D.S. Matteson, *Tetrahedron*, **45** (1989) 1859.
[48] Y. Kobayashi, T. Shimazaki, H. Taguchi and F. Sato, *J. Org. Chem.*, **55** (1990) 5324.
[49] S. Hara, *Yuki Gosei Kagaku Kyokaishi*, **48** (1990) 1125.
[50] S. Hyuga, S. Hara and A. Suzuki, *Bull. Chem. Soc. Japan*, **65** (1992) 2303.
[51] T. Amano, *Kagaku to Kogyo*, **65** (1991) 505.
[52] Y. Chujo, *Kobunshi*, **42** (1993) 560.
[53] T. Imamoto, *Yuki Gosei Kagaku Kyokaishi*, **51** (1993) 223.
[54] X.-C. Liu, J.L. Hubbard and W.H. Scouten, *J. Organomet. Chem.*, **493** (1995) 91.
[55] S. Toyota and M. Oki, *Bull. Chem. Soc. Japan*, **65** (1992) 1832.
[56] S. Toyota and M. Oki, *Bull. Chem. Soc. Japan*, **65** (1992) 2215.
[57] S. Toyota and M. Oki, *Bull. Chem. Soc. Japan*, **65** (1992) 2857.
[58] S. Toyota and M. Oki, *Bull. Chem. Soc. Japan*, **64** (1991) 1554.
[59] S. Toyota and M. Oki, *Bull. Chem. Soc. Japan*, **64** (1991) 1563.
[60] C.T. Goralski, B. Singaram and H.C. Brown, *J. Org. Chem.*, **52** (1987) 4014.

7 Organoaluminum Compounds

7.1 INTRODUCTION

Speaking of organoaluminum compounds, they are well-known compounds as one of the components of Ziegler–Natta catalysts which are used for the polymerization of olefins such as ethylene and propylene. The total production of plastics in major plastics producing countries in the world is shown in Table 7.1 [1–7]. The production amounts of polyethylene and polypropylene in the major producing countries in 1995 are around 23 million tons and 12 million tons, respectively. Total production amount of plastics in the major plastics producing countries is 81 million tons in 1995, and the production amount of plastics in the world is 120 million tons which is 1.5 times that. Then the total production amount of polyethylene and polypropylene which is produced mainly by using organoaluminum compounds as the catalyst in the world in 1995 is estimated at 52 million tons.

The major plastics producing countries are the United States, Japan, Germany, France, England, Canada, Italy, Spain, the Netherlands, Belgium, Finland and Australia.

Table 7.1 Total production (in million tons) in major plastics producing countries in the world [1–7]

Plastic	1984	1986	1988	1990	1992	1994	1995
PVC	7.512	8.075	10.238	10.442	11.345	12.738	12.411
polystyrene	3.727	4.034	5.663	5.312	5.210	7.196	6.790
ABS. AS resin	0.694	1.319	1.728	2.212	1.840	3.169	1.668
LDPE	8.147	9.156	11.313	11.412	12.663	12.550	13.104
HDPE	4.796	5.518	7.076	6.756	8.934	10.025	9.639
polypropylene	4.697	5.306	7.870	8.476	10.434	11.943	11.818
PET	—	0.539	1.288	1.451	1.842	2.197	2.870
methacrylate	1.288	1.179	1.799	1.351	0.952	1.256	0.411
polyamides	0.283	0.326	0.438	0.689	0.644	1.033	1.408
urea.melamines	1.960	1.828	2.273	2.851	2.717	2.091	2.047
phenolics	1.793	1.811	2.189	2.104	2.016	1.972	2.032
other plastics	8.584	9.266	9.191	7.622	11.064	10.167	16.483
total	46.796	51.186	66.668	65.202	73.732	82.562	80.681
total (world)	73.039	81.058	94.214	98.916	98.895	111.099	119.593

As organoaluminum compounds are used as the catalysts for producing polymers which are produced in such large quantities, even if the added amounts of the catalysts are small, it is easily estimated that considerable amounts are used, even if the total amount is unknown.

This is similar to the organotin compounds which are used as the stabilizers of polyvinyl resins. Namely, the production of polyvinyl chloride is about 12 million tons in 1995. The production amount of polyvinyl chloride is the second largest, next to polyethylene, of plastics in the world. Then, the total amount used reaches to several ten thousand tons even if the amounts used as the stabilizers are small [8].

Organoaluminum compounds are used as polymerization catalysts of butene, isoprene and butadiene besides ethylene and propylene, dimerization catalysts of linear higher α-olefins, linear higher-α-alcohols and olefins, productions of organometallic compounds such as organotin compounds and organolead compounds, productions of high purity alumina and aluminum thin film.

In recent years, articles on organosynthetic reactions using various kinds of organometallic compounds have greatly increased, many reviews have been published, and thus many reports on organoaluminum compounds have also been published. Organoaluminum compounds are easily procured since they are widely used and are thus cheap. Therefore it is estimated that their new uses would be developed successively.

7.2 ALUMINUM

The Clarke number is the amount in existence of elements in the Earth's surface, comprising 10 miles of atmosphere and hydrosphere. However, the amount of an element in the Earth's surface not containing the atmosphere and the hydrosphere is shown in Table 7.2 [9].

The largest amount is for oxygen, the second is silicon and aluminum is the element in third place, as shown in Table 7.2. However, it was very late when we began to use aluminum as a metal compared with metals such as iron, copper, silver, gold, etc. It only really dated from the nineteenth century.

Many metals are produced by the reduction of metal oxides, but work on using aluminum as the metal was very recent since the reduction of alumina was very difficult. In other words, aluminum oxide is a very stable substance.

The ore for the raw material of aluminum is generally well known as bauxite. The bauxite is a hydrate ($Al_2O_3 \cdot xH_2O$. $x = 1$–3) of alumina (Al_2O_3).

At first, in the production of aluminum the bauxite is dissolved in concentrated aqueous sodium hydroxide under high temperature and pressure, the high temperature extracted solution is cooled to crystallize $Al(OH)_3$ and subsequently $Al(OH)_3$ is burn to give pure alumina (Al_2O_3). Electrolysis using the Hall–Héroult process gives aluminum metal. The electrolyte of alumina in the Hall–Héroult process is a mixture of cryolite (Na_3AlF_6) and small amount of AlF_3. The elec-

Table 7.2 The average abundance of an element in the Earth's crust [9]

Atomic number	Atom	Average abundance (ppm)	Atomic number	Atom	Atomic abundance (ppm)
3	Li	20	46	Pd	0.0006
4	Be	2.6	47	Ag	0.07
5	B	10	48	Cd	0.11
6	C	480	49	In	0.049
7	N	25	50	Sn	2.2
8	O	474000	51	Sb	0.2
9	F	950	52	Te	0.005
11	Na	23000	53	I	0.14
12	Mg	23000	55	Cs	3
13	Al	82000	56	Ba	500
14	Si	277000	57	La	32
15	P	1000	58	Ce	68
16	S	260	59	Pr	9.5
17	Cl	130	60	Nd	38
19	K	21000	62	Sm	7.9
20	Ca	41000	63	Eu	2.1
21	Sc	16	64	Gd	7.7
22	Ti	5600	65	Tb	1.1
23	V	160	66	Dy	6
24	Cr	100	67	Ho	1.4
25	Mn	950	68	Er	3.8
26	Fe	41000	69	Tm	0.48
27	Co	20	70	Yb	3.3
28	Ni	80	71	Lu	0.51
29	Cu	50	72	Hf	5.3
30	Zn	70	73	Ta	2
31	Ga	18	74	W	1
32	Ge	1.8	75	Re	0.0004
33	As	1.5	76	Os	0.0001
34	Se	0.05	77	Ir	0.000003
35	Br	0.37	78	Pt	0.001
37	Rb	90	79	Au	0.0011
38	Sr	370	80	Hg	0.05
39	Y	30	81	Tl	0.6
40	Zr	190	82	Pb	14
41	Nb	20	83	Bi	0.048
42	Mo	1.5	90	Th	12
44	Ru	0.001	92	U	2.4
45	Rh	0.0002			

trolyte is able to dissolve alumina to about 20 % at 960–980 °C, however, usually, 5–10 % of alumina is used. The cathode is the electrolytic cell wall, and the anode is a carbon electrode rod provided from the upper part to the vessel. The electrolysis is carried out at several tens of thousands of amps to several hundred thousand

Table 7.3 Physical properties of aluminum [10–12]

Property	Value
melting point	660.2 °C
boiling point	2060 °C
crystal structure	face-centered cubic lattice
atomic radii	0.143 nm
ionic radii four coordination	0.049 nm
six coordination	0.051 nm
density	2.6989 kg/m^3 at 20 °C
lattice constant	4.0496 × 10^{-10}m at 20 °C
coefficient of expansion	23 × 10^{-6}/K at 20 °C
thermal conductivity	2.37 W cm^{-1}K^{-1} at 20 °C
electroresistivity	2.6548 × 10^{-8} Ω m
magnetic susceptibility	16 × 10^{-3} mm^{-3}mol^{-1} at 20 °C
Mohs hardness	2.75

amps. The Al_2O_3 is separated to Al and O_2 by the electrolysis. Al is accumulated on the bottom of the cathode cell wall. On the other hand, the oxygen becomes CO_2 or CO by reaction with the carbon of the upper anode. The purity of the Hall–Héroult process reaches to 99.95 % at the highest, but if we require the higher purity, we should repeat this electrolysis or we should carry out a fractional crystallization [10].

The physical properties of aluminum are shown in Table 7.3 [10–12]. Aluminum has a high electrical conductivity, a thermal conductivity and great resistances to corrosions. Aluminum is soft and lacks strength, but it can be alloyed with many other elements to increase its strength and impart a number of useful properties. Alloys of aluminum are light, strong and readily formable by many metal-working processes [10]. Although aluminum is one of the most reactive of the common commercial metals, it is remarkably stable in many oxidizing environments. It owes its stability to the continuous film of aluminum oxide, since this rapidly grows on the aluminum surface exposed to oxygen, water, or the other oxidants. The aluminum of purity greater than 99.95 % resists attack by most acids, and is stable to concentrated nitric acid, concentrated sulfuric acid and organic acids. Therefore, aluminum is used to store them as the containers. However its oxide film dissolves in alkaline solutions. Aluminum is amphoteric and can react with mineral acids to form soluble salts and evolve hydrogen, and it is dissolved in aqueous alkaline solution to evolve hydrogen to form the aluminates [12].

7.3 PREPARATION OF ORGANOALUMINUM COMPOUNDS

Trialkylaluminum compounds as representative organoaluminum compounds are prepared mainly by the following two reactions [13–16].

1 Displacement process
2 Direct process

The aluminum, which is obtained by activation treatment, reacts directly with the mixture of isobutylene and hydrogen to give triisobutylaluminum. The activation treatment is carried out by physically pulverizing it or chemically treating it with the addition of a small amount of iodine or triisobutylaluminum. The triisobutylaluminum obtained, reacts with ethylene to give triethylaluminum by replacing the isobutyl group with ethylene as shown in eq. (7.2). Hence, the displacement process is two step process of eqs. (7.1) and (7.2). This isobutylene obtained, is reused again in the reaction shown in eq. (7.1).

$$\mathrm{Al} + \tfrac{3}{2}\mathrm{H_2} + 3(i\text{-}\mathrm{C_4H_8}) \xrightarrow[50-100\ \mathrm{atm}]{130\ ^\circ\mathrm{C}} \mathrm{Al}(i\text{-}\mathrm{Bu})_3 \tag{7.1}$$

$$\mathrm{Al}\,(i\text{-}\mathrm{Bu})_3 + 3\mathrm{CH_2{=}CH_2} \xrightarrow{100\ ^\circ\mathrm{C}} \mathrm{AlEt_3} + 3(i\text{-}\mathrm{C_4H_8}) \tag{7.2}$$

In the reaction shown in eq. (7.1), if ethylene in place of isobutylene is used, triethylaluminum is obtained and this compound tends to react with hydrogen to yield the hydride. Then, as shown in the following reactions, two-step reactions, consisting of the hydride formation reaction and alkylation of the hydride, are required [15]. The reactions shown in eqs. (7.3) and (7.4) are the direct processes. The direct process produces three mole of triethylaluminum from two moles of triethylaluminum. The increased one mole is taken out as the product and two moles are recycled for the reaction [15].

$$2\mathrm{AlEt_3} + \mathrm{Al} + \tfrac{3}{2}\mathrm{H_2} \xrightarrow[100-150\ \mathrm{atm}]{100-140\ ^\circ\mathrm{C}} 3\mathrm{AlEt_2H} \tag{7.3}$$

$$3\mathrm{AlEt_2H} + 3\mathrm{C_2H_4} \xrightarrow[20-40\ \mathrm{atm}]{80-120\ ^\circ\mathrm{C}} 3\mathrm{AlEt_3} \tag{7.4}$$

In the case of using ethylene in place of the isobutylene in the reaction shown in eq. (7.1), the reaction requires a high temperature and a high pressure, and the production amount of the long chain alkylaluminum increases. But, the formation reaction of the long chain alkyl with branched olefins such as isobutylene, does not proceed easily [13]. As the other synthetic reactions of organoaluminum compounds, two reaction processes are available. The first one is the sesqui process. This process is the direct reaction of alkyl halides with aluminum. As shown in eqs.

$$(\mathrm{CH_3CH_2})_3\mathrm{Al} + \mathrm{CH_2{=}CH_2} \longrightarrow (\mathrm{CH_3CH_2})_2\mathrm{Al}(\mathrm{CH_2CH_2CH_2CH_3}) \tag{7.5}$$

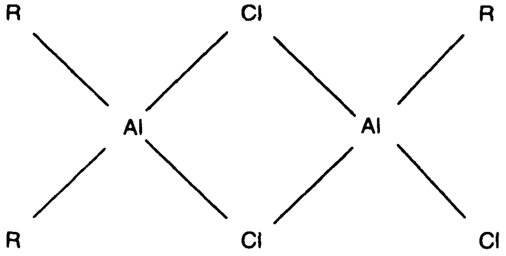
(7.6)–(7.8), methyl chloride or ethyl chloride reacts with aluminum to give alkylaluminum sesquichlorde ($R_3Al_2Cl_3$). The alkylaluminum sesquichloride is the

$$3MeCl \quad + \quad 2Al \longrightarrow Me_3Al_2Cl_3 \qquad (7.6)$$

$$3EtCl \quad + \quad 2Al \longrightarrow Et_3Al_2Cl_3 \qquad (7.7)$$

$$R_3Al \quad + \quad AlCl_3 \longrightarrow R_3Al_2Cl_3 \qquad (7.8)$$

compounds having an electron-deficient bond of halogen bridges as shown in the following formula. A small amount of mercury or iodine is used as the reaction accelerator [16]. In the reactions shown in eqs. (7.6) and (7.7), when the alkyl group of the alkyl halides are higher alkyl groups than propyl, the reaction does not proceed. Then, the preparation of the higher alkylaluminum sesquichloride are carried out with redistribution process [13]. And the preparations of dialkylaluminum chloride or alkylaluminum dichlorides are also carried out by redistribution process as shown in eqs. (7.9) and (7.10).



$$R_3Al \quad + \quad R_3Al_2Cl_3 \longrightarrow 3R_2AlCl \qquad (7.9)$$

$$R_3Al_2Cl_3 \quad + \quad AlCl_3 \longrightarrow 3RAlCl_2 \qquad (7.10)$$

As the other organometallic compounds, the five-membered ring compounds of organoaluminum compounds are prepared by cyclometalations such as lithium compounds (eq. (3.12)) and zinc compounds (eq. (5.7)) [16a,16b].

Recently pentamethylcyclopentadiene (Cp*) reacts with organoaluminum compounds to give Cp*Al, and, as shown in eq. (7.10a), the Cp*Al react with $AlCl_3$ to give an organoaluminum sandwich product $[(\eta^5\text{-Cp*})_2Al]^+[\eta^1\text{-Cp*AlCl}_3]^-$. The sandwich structure like ferrocene is found by X-ray diffraction studies [16c].

$$3Cp^*Al \quad + \quad AlCl_3 \longrightarrow [(\eta^5\text{-}Cp^*)_2Al]^+[\eta^1\text{-}Cp^*AlCl_3]^- + 2Al \qquad (7.10a)$$

7.4 PROPERTIES OF ORGANOALUMINUM COMPOUNDS

Alkylaluminums generally are thermally very stable: thus they are able to be stably stored under an inert atmosphere at ambient temperatures. Straight-chain trialkylaluminum having C_2–C_4 compounds begin to decompose slowly according to the transformation shown in eqs. (7–11) and (7–12) at ca. 100 °C. Branched-chain trialkylaluminum compounds, e.g., triisobutylaluminum, begin to decompose at *ca.* 50 °C [13]. These properties are utilized for the preparation of olefins, purification of aluminum metal and aluminum thin films [17].

$$R_3Al \xrightarrow{\text{heat}} \text{olefin} + R_2AlH \qquad (7.11)$$

$$R_2AlH \xrightarrow{\text{heat}} 2\ \text{olefin} + Al + \tfrac{3}{2} H_2 \qquad (7.12)$$

The lower alkylaluminums compounds are spontaneously flammable in air. Alkylaluminum is gradually oxidized and hydrolyzed to give alcohols [13,17,18,18a]. Alkylaluminums are freely soluble in aromatic and saturated aliphatic hydrocarbons. But, the other solvent such as ethers and t-amines forms complexes, and alkylaluminums react with water, alcohol, ketones, esters and many halohydrocarbons [13,16]. As described above, aluminum sesquichloride ($R_3Al_2X_3$), trimethylaluminum (Figure 7.1 [19,20]) and dimethylaluminum (Figure 7.2 [21]), etc. tend to associate and form the electron-deficient bond of a three-center two-electron bond. In the bridged structure, the order of the bond strength regarding hydrogen and alkyl groups is as follows:

$$R_3Al \xrightarrow{O_2} (RO)_3Al \xrightarrow{H_2O} ROH + Al(OH)_3 \qquad (7.13)$$

hydride ≫ methyl > ethyl > isopropyl > *t*-butyl

Namely, branched alkylaluminum does not tend to form the bridged structures. Therefore triisobutylaluminum exists as monomers at ambient temperatures. The elements which form bridged structure shown in Figure 7.1, are alkyl carbon, phenyl carbon (Ph_3Al [22]), hydrogen (Figure 7.2 [21]), halogen (R_2AlX, Cl, Br, I), oxygen (R_2AlOR'), nitrogen ($R_2AlNR'_2$), sulfur (R_2AlSR'), etc. [16,23].

In these associations, the alkylbridge bonds are very weak compared with the other bridge bonds of hydrogen, halogen and hetero atoms [16,24]. For example, $MeAlCl_2$ forms a dimer with the bridge bond of chlorine atom (the methyl group does not form the bridge bond [25]). The Al–H and Al–C bonds of the aluminum compounds show characteristic reactivities, and their reactivities are industrially utilized. The most representative reaction is hydroalumination. The reverse reaction is an olefin elimination. Ethylene is the most reactive of the olefins in the hydro-

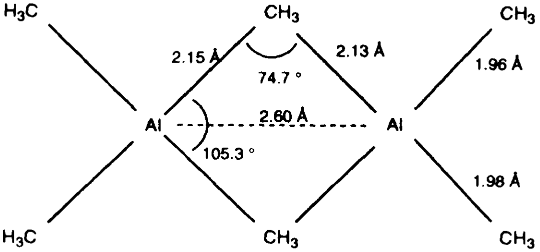


Figure 7.1. Geometry, bond distance, and bond angles in the dimeric trimethylaluminum molecule [19,20].

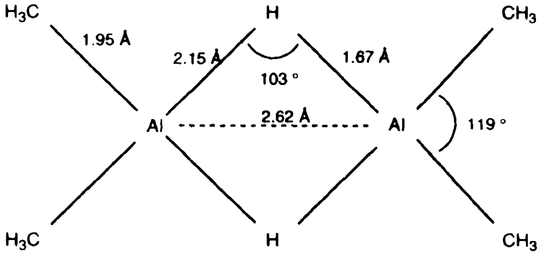


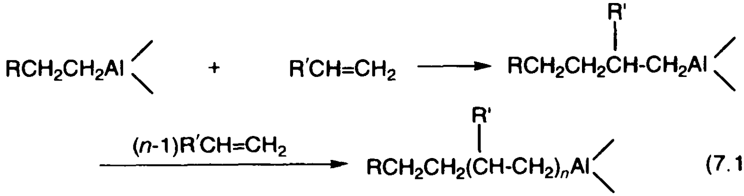
Figure 7.2. Molecular structure of the dimeric dimethylaluminum hydride by gas phase electron diffraction [21].

alumination, and the second is the other α-olefins. The reactivities of internal olefins are the lowest. The order of the reactivity is as follows [14]:

$$\mathrm{Al{-}H} + \mathrm{RCH{=}CH_2} \longrightarrow \mathrm{RCH_2CH_2Al} \qquad (7.14)$$

$$\mathrm{RCH{=}CHR} < \mathrm{R_2C{=}CH_2} < \mathrm{RCH{=}CH_2} < \mathrm{CH_2{=}CH_2}$$

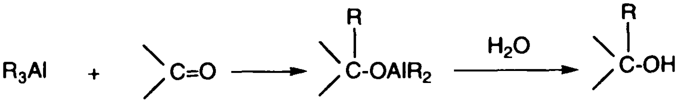
The hydroalumination is an important reaction for the production of organometallic compounds. The reverse reactions are utilized for the production of olefins. Triethylaluminum and the other trialkylaluminum compounds are able to add ethylene or the other olefins. These are carboalumination reactions. The aluminum atom mainly bonds to the terminal methylene carbon (the addition ratio of methylene carbon and methin carbon of the reaction shown in eq. (7.15) is about 9 : 1 [16]). Further olefin is added to the products successively and forms highly polymeric compounds (Ziegler growth reaction [23]), and the polymers have a molecular weight up to about 3000. It is difficult to get the higher molecular weight polymer if only alkylaluminums are used as the catalysts. The releasing reaction of olefin becomes the more active when the chain becomes the longer and the temperature is higher [17]. As alkylaluminums, their alkylations to carbonyl groups



(7.15)

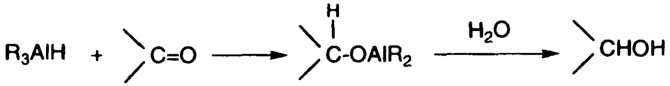
R, R' = alkyl

tend to proceed: are able to use as the alkylation agent for acyl halides, ketones, acid anhydrides, esters, lactones and aldehydes [16].



(7.16)

As organoaluminum hydrides, they act as a mild reducing agent to carbonyl groups, and they are used as the reagents for synthesizing pharmaceuticals as described below.



(7.17)

7.5 APPLICATIONS OF ORGANOALUMINUM COMPOUNDS

As to the organometallic compounds, their competitions of research and development are keen compared to petrochemical products and general polymers. Therefore, their preparation processes, production amounts and uses are confidential matters of each company, most of these are not published, hence are almost unknown. On organoaluminum compounds, the situations are the same.

The productions amount is estimated to be several ten thousand tons, however, we don't know in detail [13,16,24]. The major uses of organoaluminum compounds are following seven kinds [15].

1. High polymer catalysts
2. Production of high linear α-olefins
3. Production of high linear α-alcohols
4. Olefin dimerization
5. Production of organometallic compounds
6. Synthetic reaction of organic compounds
7. Others

As organoaluminum compounds, aluminum metal as the raw material is cheap, and organoaluminum compounds are the compounds which have been largely produced and we are able to get them relatively at low price. Further, organoaluminum compounds are as reactive as the other organometallic compounds. These have been tested for various uses. Hence, these are the most expected organometallic compounds to be used from this time on.

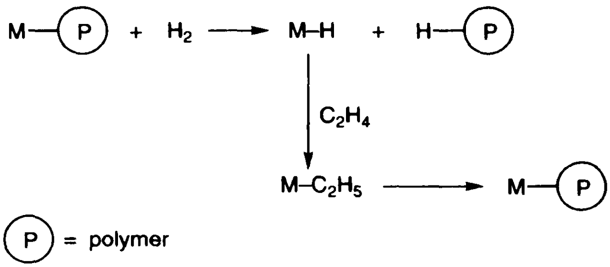
7.5.1 POLYMER CATALYSTS

Organoaluminum compounds are used as one component of the Ziegler–Natta catalysts of olefins and dienes. The polymers are, for example, polyethylene, polypropylene, etc. The Ziegler–Natta catalysts are the main group organometallic compounds of Al, Mg and Li of group 1–3 and group 11–13 in the periodic table and transition metal compounds. For example, the representative catalyst systems are as follows:

High density polyethylenes	$TiCl_4$-$AlEt_2Cl$, $TiCl_4$-$AlEt_3$
Polypropylene	$TiCl_3$-$AlEt_2Cl$
Ethylene–propylene rubbers	$VOCl_3$-$Al_2Et_3Cl_3$
Butadiene rubbers	$CoCl$-$AlEt_2Cl$

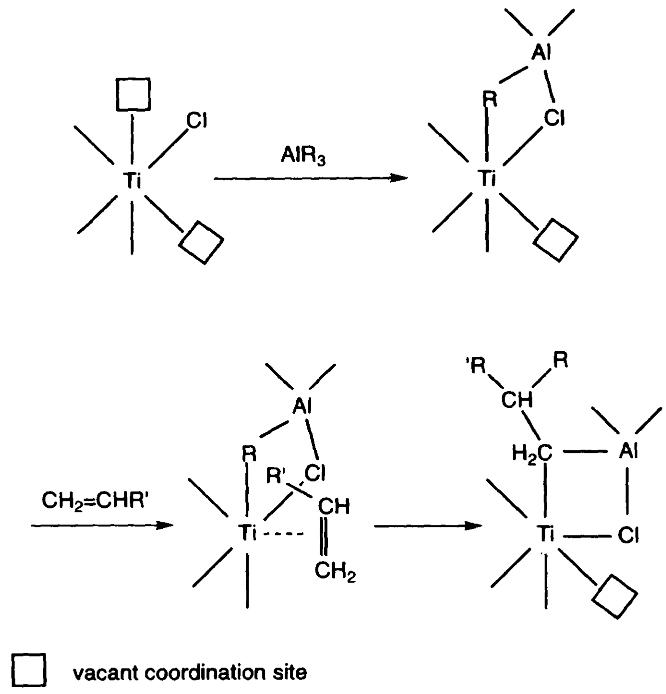
Many articles on the active center of these catalysts have been reported [26,26a]. In the alkylaluminum-titanium type catalysts, the following things are known [26].

1 It is difficult to get very high molecular weight polymers with single catalysts of alkylaluminum.
2 If the alkylaluminum labelled with ^{14}C is used, the polymer contains ^{14}C.
3 Hydrogen acts as chain transfer reagents and the number of the active centers is not decreased as shown in Scheme 7.1 [26].



Scheme 7.1 [26]

From this evidence and the reaction mechanisms of Natta [27], Cossee-Arlman [28] and Rodriguez-van Looy [29], the mechanism of the polymerization with R_3Al-$TiCl_m$ ($m = 3,4$) is considered as follows: Ti has a six-coordination structure.



Scheme 7.2 [26]

It forms bridged structure with alkylaluminum, and titanium is coordinated from one of vacant coordination sites. The bridged structure of Ti and Al gives the activation of Ti and the restriction of the direction of olefin coordination. Scheme 7.2 is shown in the polymerization of propylene [26].

Lately, a very reactive Ziegler–Natta type catalyst has been put to practical use by joint development between Mitsui petroleum chemistry and Montegison. N. Kashiwa and co-workers have reported many reviews [30–34a]. Their catalysts are $TiCl_4$–$AlEt_3$ as basic catalysts, and $MgCl_2$ as a carrier. The $MgCl_2$ has the similar crystal structure and the similar cation radius to $TiCl_3$, and the catalyst is a resulted in by sharply increasing specific surface area of titanium. Furthermore, PhCOOEt as an electron donor is added to the catalyst. By adding PhCOOEt, the stereospecificity sharply increased [31]. It is considered that the stereospecificity increased because the direct of olefin coordination is restricted since the carbonyl oxygen of the electron donor coordinates to the metal, the reactivity of this catalyst is 1,000 times or more to Natta catalyst ($TiCl_3$-$AlEt_3$) in propylene polymerizations. The isotactic polymer is obtained in 98% or more. Hence, the removal process of atactic polymer and catalyst recovery process become useless. Furthermore, granulation process is also useless since this process gives the polymer with a homogeneous grain distribution polymer and further they are able to be operated in a gas phase reaction [30,31]. Then, this process is not only for the improvement of polymer properties but also it makes great strides in the improvement of the reaction process. Furthermore as the reactivity of the catalyst of this process is high, the consumption of organoaluminum compounds should be sharply decreased.

Recently, Inoue and Aida have reported on a novel method for syntheses of a polymer with controlled molecular weight by using a metaloporphyrin. The control of molecular weight is carried out by a living polymerization, that is, the molecular weight is roughly determined by the amounts of polymerization initiator and monomer. The metaloporphyrin acts as the polymerization initiator, the central metal of the porphyrin skeleton is aluminum, titanium or zinc. When bulky Lewis acid, e.g. $MeAl(OC_6H_3(t\text{-}Bu)_3(-2,-4,-6))_2$, is added to the reaction system, Lewis acid coordinates only to the monomer and activates the monomer, then the polymerization velocity is largely increased [34f].

7.5.2 MANUFACTURES OF LINEAR HIGHER α-OLEFINS

Trietylaluminum is stepwise added to ethylene (carboalumination reaction) to give a polymeric trialkylaluminum. This polymeric trialkylaluminum is substituted by ethylene with heating or in the presence of nickel salt, and the high linear α-olefin is liberated as shown in eq. (7.18) [15]. The molecular weights of high linear α-olefins

$$AlEt_3 + 3nC_2H_4 \xrightarrow[100\ \text{atm}]{120\ ^\circ\text{C}} Al((C_2H_4)_nEt)_3$$

$$\xrightarrow[\text{heat}]{3C_2H_4} 3C_2H_5(C_2H_4)_{n-1}CH{=}CH_2 + AlEt_3 \tag{7.18}$$

vary according to the reaction conditions. The uses of these products are as follows [35].

Comonomer of linear low density polyethylene	C_4, C_6, C_8
Higher alcohol for plasticizers	C_6, C_8, C_{14}
Higher alcohol for detergents	C_{10}, C_{12}
Lubricant additives	C_{14}, C_{16}, C_{18}
Olefin oxides	C_{12}–C_{30}
Substituted olefin waxes	$\geqslant C_{30}$

High linear α-olefins were used as the raw materials of higher alcohols in the oxo process or of synthetic detergents. Recently, the demand of linear low density polyethylene copolymers having high strength, high impact strength and high heat resistance have been increased. The demand of higher linear α-olefins in the world was 800×10^3 tons in 1990. It is estimated to increase to 1700×10^3 tons in 2000 [35].

7.5.3 HIGH LINEAR α-ALCOHOLS

The intermediate product of the production of high linear α-olefins is a high linear trialkylaluminum ($Al(C_2H_4)_nEt)_3)$) and the long linear α-alcohol is prepared by an oxidation with air and a hydrolysis [15].

$$Al((C_2H_4)_nEt)_3 + \frac{3}{2}O_2 \longrightarrow Al(O(C_2H_4)_nEt)_3$$

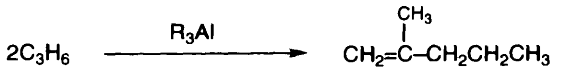
$$\xrightarrow{H_2O} 3Et(C_2H_4)_nOH + Al(OH)_3 \qquad (7.19)$$

Hitherto highly linear α-alcohols were manufactured by the reduction of animals or plants oil. However, they have cheaply manufactured with petrochemicals as raw materials by the above reactions [15]. For example, butanol is prepared in 88% yield by the air oxidation of tributylaluminum in toluene at 40 °C, followed by hydrolysis with 10% aqueous sulfuric acid [35,36].

$$Bu_3Al \xrightarrow[\text{in toluene}]{40\ ^\circ C,\ O_2(air)} (BuO)_3Al \xrightarrow{10\ \%\ H_2SO_4} 3BuOH \qquad (7.20)$$

7.5.4 DIMERIZATION OF OLEFINS

Alkylaluminum reacts with ethylene as a single catalyst to give the high molecular alkyl compounds. However, with propylene or butene, the reaction is dimerization accompanied by a releasing reaction, and hexene or octene is obtained [15].



$$2C_3H_6 \xrightarrow{R_3Al} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2CH_2CH_3 \qquad (7.21)$$

$$2C_4H_8 \xrightarrow{R_3Al} CH_2{=}\overset{Et}{\overset{|}{C}}{-}CH_2CH_2CH_2CH_3 \qquad (7.22)$$

Hexene (2-methylpentene-1) which is the dimer of propylene, gives heptanol, which is the raw materials of plasticizers in the oxo process [15].

7.5.5 MANUFACTURES OF ORGANOMETALLIC COMPOUNDS

Organoaluminum compounds are cheap compounds compared to organometallic compounds described above, and they have also a high reactivity. Then, they are available for the raw materials of organometallic compounds. For example, tetraalkyltin, as organotin compounds, is prepared as follows [37].

$$4R_3Al + 3SnCl_4 + 4NaCl \longrightarrow 3R_4Sn + 4NaAlCl_4 \qquad (7.23)$$

By using an excess of $SnCl_4$ for preparation of organotin chloride, the monochloride and the dichloride are prepared by the reaction shown in eqs. (7.24) and (7.25).

$$R_3Al + SnCl_4 \longrightarrow R_3SnCl + AlCl_3 \quad (7.24)$$

$$2R_3Al + 3SnCl_4 \longrightarrow 3R_2SnCl_2 + 2AlCl_3 \quad (7.25)$$

Tetraethyllead is produced by the following two processes [38]. One process is an electrolytic one, using $NaAlEt_4$ as an electrolyte developed by Karl Ziegler as shown in eq. (7.26) [39,40], and the other is the reaction with $Pb(OAc)_4$ as shown in eq. (7.27) [41).

$$Pb + 2H_2 + 4C_2H_4 \xrightarrow[96\text{-}97\ \%]{NaAlEt_4} Et_4Pb \quad (7.26)$$

$$3Pb(OAc)_4 + 4Et_3Al \xrightarrow[\text{in toluene}]{95.8\ \%} 3Et_4Pb + 4Al(OAc)_3 \quad (7.27)$$

Organozinc compounds and organoboron compounds are also prepared with organoaluminum compounds as shown in eqs. (7.28) and (7.29) [15].

$$ZnCl_2 + 2AlR_3 \longrightarrow ZnR_2 + 2AlR_2Cl \quad (7.28)$$

$$BF_3 + R_3Al \xrightarrow{KF} R_3B + AlF_3 \quad (7.29)$$

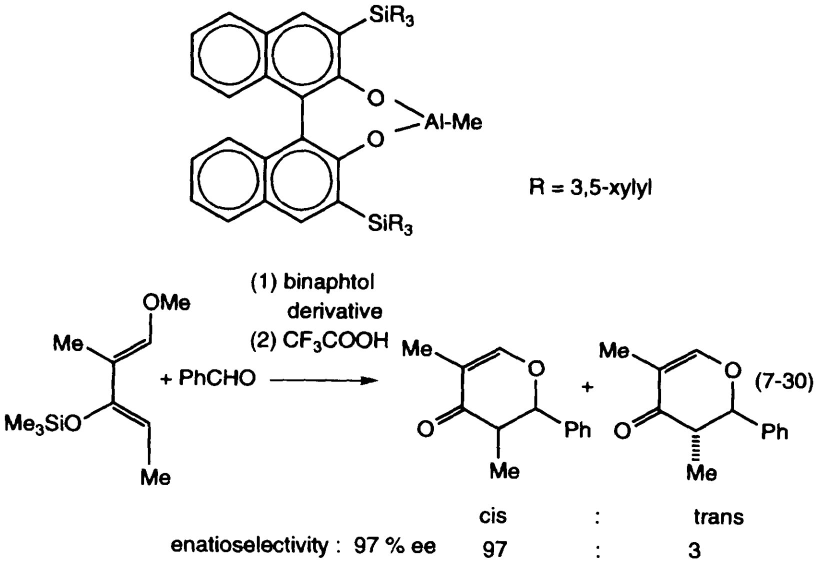
7.5.6 PREPARATIVE REACTIONS OF ORGANIC COMPOUNDS

The aluminum atom in organoaluminum compounds has a vacant p orbital, and it is a Lewis acid which is able in its turn to form a coordination bond with a weak base such as ether. In the Al-C bond of the organoaluminum compounds, the difference of electronegativities of the two atoms ($C=2.50$, $Al=1.49$) is large. Then, the carbon acts as a carbanion. Namely, organoaluminum compounds have two properties of the Lewis acid of aluminum atom and of the nucleophilicity of alkyl or aryl ligand. Further, they form the ate complexes with anionic reagents such as alkyllithiums (for example, LiEt and $AlEt_3$ forms $Li^+(AlEt_4)^-$), and they are used as a powerful nucleophilic reagent.

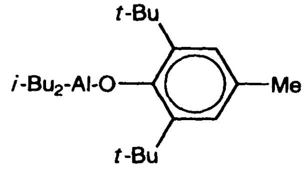
Organoaluminum compounds have a strong affinity to oxygen atoms. They tend to form a relatively stable coordination bond. Therefore, organoaluminum compounds having a bulky group are used as highly stereospecific reagents by forming intermediates bonded with the oxygen containing compounds to form less hindered side [42–53].

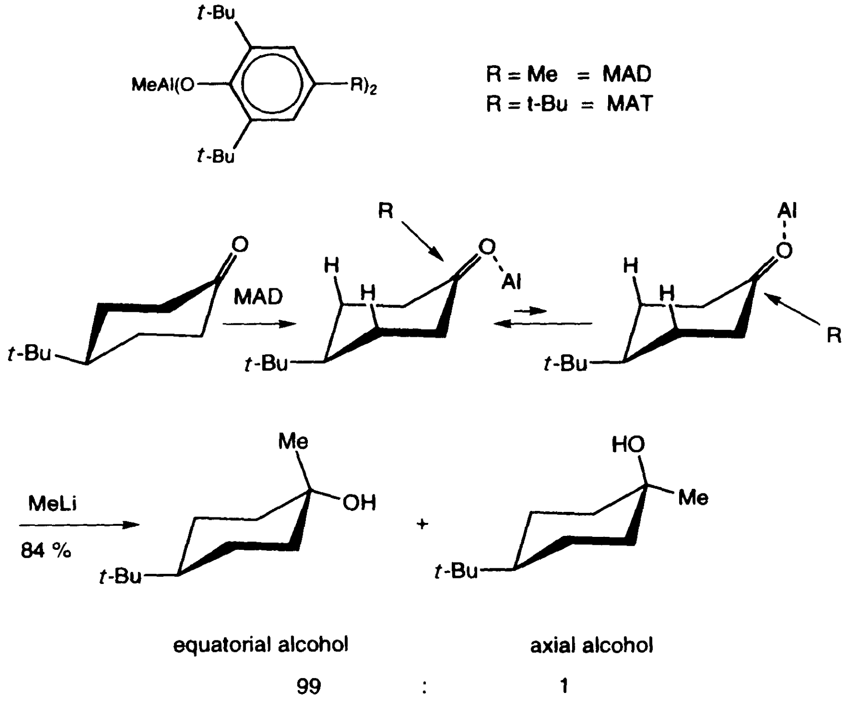
For example, the aluminum compounds of 2,6-di-t-butylphenol derivatives (see Scheme 7.3, MAD, MAT), react with cyclohexane derivatives to give equatorial alcohol of a highly steric hindrance via a less hindered coordination intermediate (99 % with MAP, 99.5 % with the more bulky MAT) [44,49]. But the reaction with MeLi alone gives a less hindered axial alcohol as the main product (79 %) [44].

In the Diels–Alder reaction of siloxydiene with benzaldehyde in the presence of an organoaluminum compound having an optical active bulky binaphthol as shown in eq. (7.30), the reaction proceeds via the intermediate burst of aluminum coordinated with carbonyl oxygen of benzaldehyde. As the aluminum is bonded with two naphthalene bond with bulky Si(3,5-xylyl)$_3$, the highly stereospecific product is obtained by the restriction of the reaction direction of dienes [44,45,49,49a].



Organoaluminum compounds are available as mild reducing agents for vitamins, hormones and the other pharmaceuticals [15]. For example, diisobutyl(2,6-di-t-butyl-4-methylphenoxy)aluminum is able to selectively reduce the keto carbonyl group of prostaglandins having esters carbonyl, carbon-carbon double bond and lactone ring to OH [54].





Scheme 7.3 [44–49]

7.5.7 OTHERS

Organoaluminum compounds are also used for obtaining highly pure alumina, aluminum nitride and aluminum thin film [15]. Alumina is the raw materials of aluminum metal and is widely used for a raw material of ceramics. Recently the development of high efficiency ceramics have been actively studied and it requires highly pure alumina.

Organoaluminum compounds are very pure raw materials for a single metal component. Organoaluminum compounds are hydrolyzed to give aluminum hydroxide, and oxidized to give highly pure alumina. Thus highly pure special alumina is available for abradants and a highly pure sintering agent since it forms homogeneous fine particles and has an excellent sintering property [15,55]. Fine ceramics using aluminum, is using aluminum nitride (AlN) besides highly pure alumina. AlN has not only a heat-resistance and a corrosion resistance as ceramics but also a high heat conduction and a high dielectric strength. Hence, AlN attracts public attention as a material for high heat conducting base. The production of AlN is by a direct nitrogenation (eq. (7.31)), alumina reduction (eq. (7.32)) and alkylaluminum process (eq. (7.33)). By the third alkylaluminum process a highly pure AlN is easily prepared [55a].

$$2Al + N_2 \longrightarrow 2AlN \qquad (7.31)$$

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO \qquad (7.32)$$

$$AlR_3 + NH_3 \longrightarrow AlN + 3R\text{-}H \qquad (7.33)$$

Recently, organometallic compounds have been used for the preparation of metal thin films. This reason is the same as in the alumina. Namely, organoaluminum compounds tend to be obtained as a highly pure substance than metal aluminum or aluminum compounds as metal components. The representative thin film formation method with organometallic compounds as the raw materials is MOCVD (Metal Organic Chemical Vapor Deposition) process [56–59]. Hydrogen is used as the carrier gas of organometallic compounds, and crystal of compounds precipitated by decomposition on the heat plate and form thin metal films. The characteristics of MOCVD is the easy control of film formation, and it is suitable for crystal increment and multi-layer formation and it is easy to form wide homogeneous film. Organoaluminum compounds for this process are Me_3Al, Et_3Al, Bu_3Al, Me_2AlN, $Me_2AlN{\cdot}NMe_3$, $Et_2AlN{\cdot}NMe_3$, etc. [57–59].

Finally, since organoaluminum compounds are cheap, show characteristic reactivity, have no problem on environmental pollution and the deposit of aluminum is much, they are expected to be developed more as organometallic compounds successively in the future.

REFERENCES

[1] *Plastics Age*, **32** Dec (1985) 99.
[2] *Plastics Age*, **34** Dec (1987) 149.
[3] *Plastics Age*, **36** Dec (1989) 185.
[4] *Plastics Age*, **38** Dec (1991) 147.
[5] *Plastics Age*, **40** Dec (1993) 116.
[6] *Plastics Age*, **42** Dec (1995) 157.
[7] Plastics Age, **43** Dec (1996) 133.
[8] I. Omae, *Kagaku Kogyo*, **41** (1990) 944.
[9] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
[10] Ullmann's *Encylopedia of Industrial Chemistry*, VCH, Weinheim, vol. A1 p. 459, 1990.
[11] *Aluminum Atsuenhin Pocket Book*, Nippon Aluminum Renmei, 1990.
[12] *Kagaku Daijiten*, Tokyo Kagaku Dojin, p. 122, 1989.
[13] Kirk-Othmer, *Encylopedia of Chemical Technology*, 3rd. ed. John Wiley and Sons vol 16, p. 555, 1980.
[14] *11691 no Kagaku Shohin*, Kagaku Kogyo Nipposha, p. 727, 1991.

[15] K. Tsukada, *Kagaku to Kogyo*, **30** (1977) 861.

[16] Ullmann's *Encylopedia of Industrial Chemistry*, VCH, Weinheim, vol. A1 p. 543, 1990.

[16a] L. Contreras, A.H. Cowley, F.P. Gabbai, R.A. Jones, C.J. Carrano and M.R. Bond, *J. Organomet. Chem.*, **489** (1995) C1.

[16b] U. Dümichen, K.H. Thiele, T. Gelbrich and J. Sieler, *J. Organomet. Chem.*, **495** (1955) 71.

[16c] C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider and R. Ahlrichs, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 1655.

[17] *Yukikinzoku no Kagaku to Oyo*, Asakura Shoten, p. 178, 1962.

[18] R.F. Schultz, *Metal-Organic Compounds*, American Chemical Society, p. 163, 1957.

[18a] S. Nozakura, *Yukikinzoku no Kagaku*, Kagaku Zokan 23, p. 279, 1966.

[19] R.G. Vranka and E.L. Amma, *J. Am. Chem. Soc.*, **89** (1967) 3121.

[20] P.H. Lewis and R.E. Rundle, *J. Chem. Phys.*, **21** (1953) 986.

[21] G.A. Anderson, A. Almenningen, F.R. Forgaard and A. Haaland, *J. Chem. Soc. Chem. Commun.*, (1971) 480.

[22] J.F. Malone and W.S. McDonald *Chem. Commun.*, (1967) 444.

[23] J.J. Eisch, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Oxford Pergamon Press, vol. 1, p. 555, 1982.

[24] Ch. Elschenbroich and A. Salzer, *Organometallics*, VCH, Weinheim, 1989.

[25] G. Allegra, G. Perego and A. Immirzi, *Makromol. Chem.*, **61** (1963) 69.

[26] P.D. Gavens, M.Bottrill, J.W. Kelland and M. McMeeking, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Oxford Pergamon Press, vol.3, p. 475, 1982.

[26a] G. Henrici-Olive and S. Olive, *Chemtech*, December (1981) 746.

[27] G. Natta and G. Mazzanti, *Tetrahedron*, **8** (1960) 86.

[28] P. Cossee, *Tetrahedron Lett.*, 17 (1960) 12; E.J. Arlman and P. Cossee, J. Catal. 3 (1964) 80, 89, 99; P. Cossee, *Recl. Trav. Chim. Pays-Bas.*, **85** (1966) 1151.

[29] L.A.M. Rodriguez and H.M. van Looy, *J. Polymer. Sci. (A-I)*, **4** (1966) 1951, 1971.

[30] N. Kashiwa and M. Kioka, *Kagaku Kogyo*, **36** (1985) 523.
N. Kashiwa and J. Yoshitake, *Makromol. Chem. Rapid. Commun.*, **3** (1982) 211.

[31] N. Kashiwa, A. Toyota and M. Kioka, *Nikakyo Geppo*, July(1985)17.

[32] H. Mineshima, N. Kashiwa, H. Koda, M. Ichimura and A. Kato, *Kagaku Kogaku*, **50** (1986) 377.

[33] N. Kashiwa and A. Toyoda, *Kagaku Keizai*, October (1986) 18.

[34] R. Ishioka and T. Sasaki, *Kagaku Meizai*, May (1990) 84.

[34a] M. Kioka, K. Hirose and N. Kashiwa, *Kagaku Kogaku*, **56** (1992) 629.

[34b] T. Aida and S. Inoue, *Yuki Gosei Kagaku Kyokaishi*, **43** (1985) 300.

[34c] S. Inoue and T. Aida, *Gendai Kagaku*, Jan (1985) 14.

[34d] T. Aida and S. Inoue, *Kobunshi*, **35** (1986) 1014.

[34e] S. Inoue and H. Sugimoto, *Shokubai*, **33** (1991) 545.

[34f] T. Aida, *Kagaku Kogyo*, **44** (1993) 554.

[35] Kagaku Kogyo Jiho, January 25, 1990.

[36] Japan Patent 59-1715 (1984).

[37] I. Omae, *Organotin Chemistry*, ed. J. Organometallic Chemistry Library **21**, Elsevier, Amsterdam, 1989.

[38] I. Omae, *Kagaku Kogyo*, **42** (1991) 579.

[39] W.P. Neumann and K. Kühlein, *Ad. Organomet. Chem.*, **7** (1968) 241.

[40] K. Ziegler and Lehmkuhl, *Angew. Chem.*, **67** (1955) 424.
K. Ziegler, *Angew. Chem.*, **71** (1959) 628; **72** (1960) 565.

[41] F.W. Frey, Jr. And S.E. Cook, *J. Am. Chem. Soc.*, **82** (1960) 530.

[42] S. Nakai and H. Yamamoto, *Yuki Gosei Kagaku Kyokaishi*, **44** (1986) 700.

[43] K. Utimoto, *Yuki Gosei Kagaku Kyokaishi*, **41** (1983) 792.
T. Mole, E.A. Jeffery, *Organoaluminum Compounds*, Elsevier, Amsterdam, 1972.

[44] H. Yamamoto and K. Maruoka, *Pure Appl. Chem.*, **60** (1988) 21.

[45] K. Maruoka and H. Yamamoto, *Yukagaku*, **39** (1990) 852.

[46] H. Yamamoto and K. Maruoka, *Pharumasia*, **20** (1984) 766.
L.A. Paquette, *Asymmetric Synthesis*, J.D. Morrison, ed., Academic Press, New York, 1984, vol. 3B, p. 455.

[47] H. Yamamoto and K. Maruoka, *Pure Appl. Chem.*, **55** (1983) 1853.

[48] K. Maruoka and H. Yamamoto, *Yuki Gosei Kagaku Kyokaishi*, **43** (1985) 429.
H. Yamamoto and H. Nozaki, *Angew. Chem. Int. Ed. Engl.*, **17** (1978) 169.

[49] K. Maruoka and H. Yamamoto, *Tetrahedron*, **44** (1988) 5001.

[49a] K. Maruoka, A.B. Concepcion and H. Yamamoto, *Bull. Chem. Soc. Japan*, **65** (1992) 3501.

[50] T.L. Macdonald and W. Clark Still, *J. Am. Chem. Soc.*, **97** (1975) 5280.

[51] K. Maruoka, T. Ito, M. Sakurai, K. Nonoshita and H. Yamamoto, *J. Am. Chem. Soc.*, **110** (1988) 3588.

[52] K. Maruoka, T. Ito, T. Shirasaka and H. Yamamoto, *J. Am. Chem. Soc.*, **110** (1988) 310.

[53] H. Yamamoto, K. Maruoka, K. Furuta and Y. Naruse, *Pure Appl. Chem.*, **61** (1989) 419.

[54] *Japan Patent*, No 62-887 (1987).

[55] S. Hirano, *Kino Zairyo*, March (1984) 1.

[55a] K. Wakimura and A. Hiai, *Kino Zairyo*, **11** Feb (1991) 13.

[56] M. Tezuka and T. Yajima, *Kagaku Kogyo*, **40** (1989) 642.

[57] A. Nishimoto, JETI, **38** (10) (1990) 75.

[58] A. Nishimoto, JETI, **38** (11) (110) 119.

[59] A. Nishimoto, JETI, **38** (12) (1990) 99.

8 Organosilicon Compounds

8.1 INTRODUCTION

Tetraethyllead has been used as a gasoline antiknock agent. However, recently the regulation of exhaust fumes from automobiles has become strict in advanced countries. Thus the uses of tetraethyllead are sharply restricted and its consumption has been decreasing remarkably. On the other hand, the consumption of organosilicon compounds has been increasing every year: it was 0.6 million tons or more in 1994 in the world. Now, organosilicon compounds account for most of the organometallic compounds used in the world [1,1a].

The major products containing Si are silicones† which are polymeric compounds having Si–O bonds. Silicones are used in various industrial fields such as the electric and electronic industries, business machinery and tools, constructions, foods, medical treatments, fibers, plastics, papers, pulps, paints, rubbers, etc. The kind of goods manufactured are three thousand or more, and increasing all the time [2]. Therefore, the number of patent applications for silicones and silanes are many and there are 4000–5000 per year in Japan. The field of organosilicon compounds is the most active of the organometallic compounds [2].

8.2 SILICON

Silicon is a member of group 14 similar to carbon in the periodic table. The outer electrons are $3s^2 3p^2$. Silicon exists in 27.70 % in the lithosphere and it is the second most abundant element after oxygen (47.40 %) [3].

Silicon does not exist in it natural elemental form. It exists mainly as an oxide (SiO_2). The ores containing silicon are quartzite and silica sand. Silicon is produced by the reduction of these ores in the electric furnace at 2000 °C or higher with coke.

$$SiO_2 + 2C \longrightarrow Si + 2CO \qquad (8.1)$$

Aluminum is also used as a reducing agent besides coke. As the reaction with aluminum is exothermic, it is carried out at 600–1800 °C [4]. The purity of metal

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† As the basic skeleton of silicones was considered at first to be $R_2Si{=}O$ similar to ketone, they were called silicoketone, and they became silicones for short.

silicon produced by these processes is 98% [5]. In order to obtain a highly pure silicon such as four nine (99.99%), nine nine and eleven nine, metal silicon is reacted with hydrogen chloride gas in the chlorination furnace to give $HSiCl_3$, and polycrystalline highly pure silicons are obtained by hydrogen reduction of $HSiCl_3$.

$$3SiO_2 + 4Al \longrightarrow 3Si + 2Al_2O_3 \quad (8.2)$$

$$Si + 3HCl \longrightarrow HSiCl_3 + H_2 \quad (8.3)$$

$$4HSiCl_3 + 2H_2 \longrightarrow 3Si + SiCl_4 + 8HCl \quad (8.4)$$

$$SiCl_4 + H_2 \longrightarrow HSiCl_3 + HCl \quad (8.5)$$

The polycrystalline silicons are also obtained by thermal decomposition of SiH_4 prepared by the reduction of Mg_2Si with hydrochloric acid or by the reduction of $SiCl_4$ with LiH at about 700°C.

$$SiH_4(g) \longrightarrow Si(s) + 2H_2(g) \quad (8.6)$$

In order to display its function as the semiconductor with these highly pure silicons, a small amount of additives are required to be added to the silicon for each of the semiconductors, and each single crystal silicon is produced.

Silicon is very resistant to ordinary acid, but not to a mixture of HF and HNO_3. Silicon reacts violently with even dilute alkaline solutions to generate hydrogen and to form SiO_4^{4-} [4]. Silicon is stable at ordinary temperatures in air. However, on heating it forms an SiO_2 layer than inhibits further oxidation. Silicon reacts with acids at 900°C or higher, with nitrogen at 1400°C or higher, with chlorine at 300°C or higher, bromine or iodine at about 500°C or higher [4,6–8]. The properties of silicon are shown in Table 8.1 [4].

8.3 PREPARATION OF ORGANOSILICON COMPOUNDS

Most of the organosilicon compounds are prepared by the following five reactions [9,10].

(1) Direct reactions
(2) Reactions with organometallic compounds
    (i) Grignard reactions
    (ii) Reactions with organoalkali metal compounds or with alkali metals
    (iii) Reaction with other organometallic compounds
(3) Hydrosilylation (addition reaction)
(4) Substitution with Si–H bond
(5) Substitution with Si–Cl bond

Table 8.1 Properties of silicon [4]

Property	Value
melting point, °C	1414
boiling point, °C	3231
crystal structure	diamond
density, at 300K, g/cm^3	2.329
specific heat, at 300K, Jg^{-1}K^{-1}	0.713
thermal expansion, at 300K, K^{-1}	2.6×10^{-6}
thermal conductivity, at 300K, W cm^{-1} K^{-1}	1.5
hardness	
Vickers, GPa	10.2
Mohs	7
latent heat of fusion, kJ/mol	50.66
heat of evaporation, kJ/mol	385
band gap, at 300K, eV	1.1
electron mobility, cm^{2}V^{-1}s^{-1}	1440
hole mobility, cm^{2}V^{-1}s^{-1}	484

8.3.1 DIRECT REACTIONS

The direct reaction process is also called the Rochow process, and methylchlorosilane and phenylchlorosilane have been industrially produced by this process [11]. Copper is used as a catalyst. However, the reaction with the single catalyst of copper is not so fast, and the addition of a metal such as Sb, Cd, Al, Zn and Sn or a mixture accelerates the reaction. For example, with a catalyst containing 94.49 wt % Si, 5.00 wt % Cu, 0.50% Zn and 0.001 % Sn, the selectivity of Me_2SiCl_2 is 80 mole %. In the reaction with methylchloride, the reaction temperature is preferably 300 °C and the conversion of silicon is 90–98 % [9].

$$Si + RX \xrightarrow[]{\substack{250-320\ °C \\ Cat.}} R_3SiX + R_2SnX_2 + RSiX_3, \text{ etc.} \qquad (8.7)$$

R = Me, Cat. = Cu,
R = Ph, Cat. = Ag
X = F, Cl, etc.

8.3.2 REACTION WITH ORGANOMETALLIC COMPOUNDS

8.3.2.1 Grignard Reactions

In Grignard reactions, $SiCl_4$, $HSiCl_3$ or organosilicon compounds are used as raw materials. For example, in the case of $HSiCl_3$, the reaction is as shown in eq. (8.8). On the other hand, in using monoalkyl silicon compounds, the reaction with aromatic compounds is shown in eq. (8.9) [9].

$$HSiCl_3 + RMgX \longrightarrow MgXCl + RSiHCl_2 + R_2SiHCl + R_3SiH \quad (8.8)$$

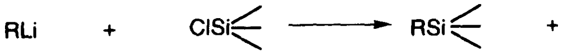
$$RSiCl_3 + ArMgX \longrightarrow MgXCl + RSiArCl_2 + RSiAr_2Cl + RSiAr_3 \quad (8.9)$$

Ar = Aryl

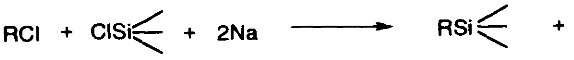
Grignard reactions are slow with a compound having a bulky organic group with much steric hindrance, but the Grignard reactions tend to substitute the halogen almost perfectly if the organic group has no steric hindrance. The reactivity of the organosilicon compounds bonded with an alkoxy group is lower than that of compounds bonded with halogen [9,10].

8.3.2.2 Reactions with Organoalkali Metal Compounds or with Alkali Metals

Organolithium compounds or sodium metal reacts with halosilanes to give organosilicon compounds. The synthetic reactions are shown in eqs. (8.10) and (8.11).



(8.10)



(8.11)

In the case of sodium metal, organosilicon compounds are prepared by a Wurtz type reaction as shown in eq. (8.11). As described above, the Grignard reaction is difficult with an organic group having bulky groups, but these Wurtz type reactions proceed easily. Hence, these reactions are applied for the reactions where the application of the Grignard reaction is difficult [9]. In the reaction using organolithium compounds, not only the substitution with halogen but also the substitution with Si–OR or Si–H proceed to give organosilicon compounds [9].

8.3.2.3 Reactions with the Other Organometallic Compounds

As organometallic compounds, organozinc compounds, organoaluminum compounds or organomercury compounds also react with halosilanes to give organosilicon compounds. However, these compounds are almost never used because of their high toxicities or low reactivities [9,10]. The reaction with organozinc compounds are shown in eq. (8.12) [9,10].

$$2R_2Zn + SnCl_4 \longrightarrow R_4Si + 2ZnCl_2 \quad (8.12)$$

8.3.3 HYDROSILYLATIONS

Hydrosilylations are the reactions in which silanes are added to olefins or acetylenes. Hydrosilylations are able to proceed at high temperatures and pressures in the absence of catalysts. However, usually the reactions are carried out with catalysts. It is considered that, with UV or γ-radiation and a peroxide as the catalysts, radical reactions proceed. On the other hand, with tertiary amines and platinum or palladium compounds as the catalysts, ionic reactions proceed. In particular, platinum catalysts show high reactivities, and the side reaction of olefin polymerization is small [10,12]. The reactions with olefins and acetylenes are shown in eqs. (8.13) and (8.14), respectively.

(8.13)

(8.14)

8.3.4 SUBSTITUTION REACTIONS WITH Si–H BONDS

On chlorosilanes having Si–H bond, dehydrochlorination reactions with hydrocarbons at high temperatures proceed. The reactions proceed at atmospheric pressure in the absence of catalysts. The dehydrochlorination reaction shown in eq. (8.16) is used as the industrial preparation method and the yield is 60–70% [9,10,12]. Substitution reactions of chlorosilanes with hydrocarbons proceed in a sealed tube at about 400 °C or in the presence of a Friedel–Crafts catalyst such as $AlCl_3$ and BCl_3 at about 230 °C (for example, eq. (8.17)) [9,10].

$$HSiCl_3 + PhCl \xrightarrow{500-600\ ^\circ C} PhSiCl_3 + HCl \quad (8.15)$$

$$MeHSiCl_2 + PhCl \xrightarrow{500-600\ ^\circ C} PhMeSiCl_2 + HCl \quad (8.16)$$

$$Ph\text{-}H + HSiCl_3 \longrightarrow PhSiCl_3 + H_2 \quad (8.17)$$

8.3.5 SUBSTITUTION REACTIONS WITH Si–Cl BONDS

Organoalkoxysilanes, acyloxysilanes and silazanes, etc., are important compounds as cross-linking agents for preparation of the various kinds of silicon polymers. They are prepared by substitution of the chlorine of methylchlorosilane with alcohols, acetic acid anhydride or amines as shown in eqs. (8.18)–(8.20), respectively [10].

$$MeSiCl_3 + 3MeOH \longrightarrow MeSi(OMe)_3 + HCl \qquad (8.18)$$

$$MeSiCl_3 + 3Ac_2O \longrightarrow MeSi(OAc)_3 + 3AcCl \qquad (8.19)$$

$$Me_3SiCl + 2PhNH_2 \longrightarrow Me_3SiNHPh + PhNH_2{\bullet}HCl \qquad (8.20)$$

8.4 REACTIONS OF ORGANOSILICON COMPOUNDS

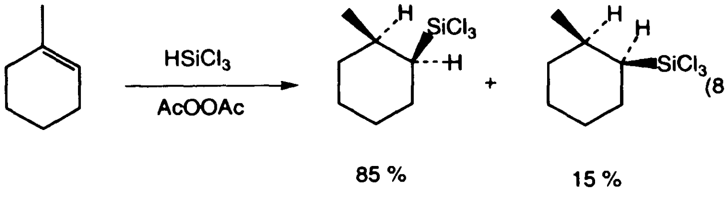
Representative reactions of organosilicon compounds are the following six.

(1) Hydrosilylations
(2) Redistribution reactions
(3) Reactions of organosilylenes
(4) Rearrangements
(5) Polymerizations
(6) Organosynthetic reactions with organosilicon compounds

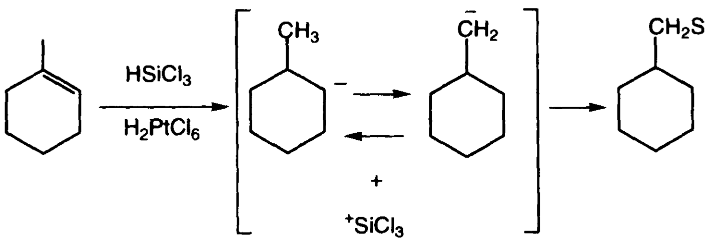
Since the organosynthetic reactions with organosilicon compounds are described below, the description of these are omitted in this section.

8.4.1 HYDROSILYLATIONS

In the hydrosilylation as described in the previous section, both the radical reaction and the ionic reaction proceed. The radical reaction with a peroxide catalyst and ionic reaction with a platinum catalyst are shown in eqs. (8.21) and (8.22), respectively [13,14].

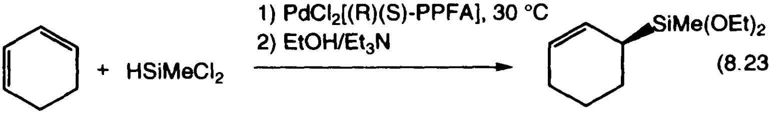


(8.21)



(8.22)

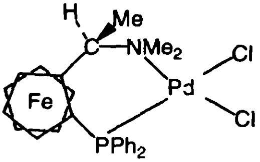
As hydrosilylation catalysts, palladium, chromium, cobalt, rhodium and ruthenium, besides platinum, are also used. The additions of silanes to dienes with these catalysts are called 1,4-addition, for example, the reaction is shown in eq. (8.23) [14–17].



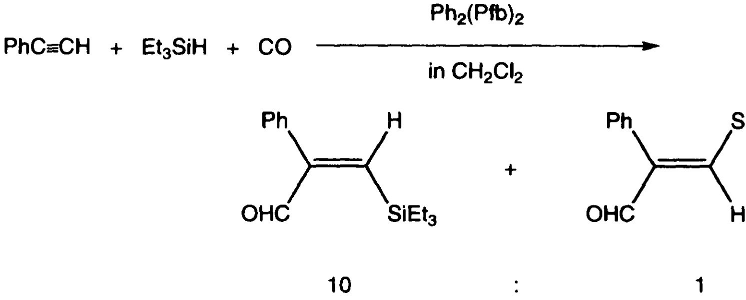
(8.23)

95 %

(R)(S)PPFA :



Hydrosilylations with transition metal catalyst tend to be a cis-addition [14]. Recently, by Doyle and Shanklin, hydrosilylation to acetylene is carried out in the presence of carbon monoxide to give Z-alkenealdehyde in high yield as shown in eq. (8.24). Rhodium is used as the catalyst and since this hydrosilylation is hydroformylation, it is called silylcarbonylation [18].



(8.24)

10 : 1

Yield = 82 %

silylcarbonlation / hydrosilyation = > 99/1

$Ph_2(Pfb)_2$ = dirhodium (II) perfluorobutyrate

8.4.2 REDISTRIBUTION REACTIONS

The redistribution reaction is also called the disproportionation reaction. The major raw material of dimethyldichlorosilanes is prepared by the direct process shown in eq. (8.7). The by-products are $MeSiCl_3$ and Me_3SiCl. These compounds react with heating in the presence of catalytic amount of aluminum chloride to give the dimethyldichlorosilane as shown in eq. (8.25). On the other hand, the reaction shown in eq. (8.26) also produce it. These two reactions are redistribution reactions, both of which are used industrially [9,10].

$$MeSiCl_3 + Me_3SiCl \underset{}{\overset{AlCl_3}{\rightleftharpoons}} 2Me_2SiCl_2 \qquad (8.25)$$

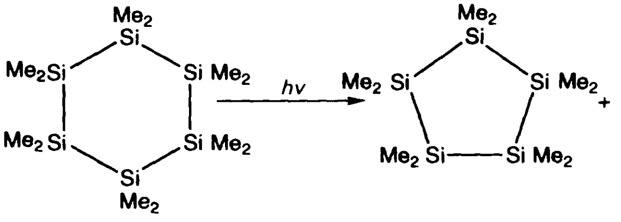
$$Me_4Si + SiCl_4 \underset{}{\overset{AlCl_3}{\rightleftharpoons}} 2Me_2SiCl_2 \qquad (8.26)$$

8.4.3 REACTIONS OF ORGANOSILYLENES

Dimethylsilylenen is prepared by the reduction of dimethyldichlorosilane with Na–K, Na or Li in a gas phase or a liquid phase as shown in eq. (8.27).

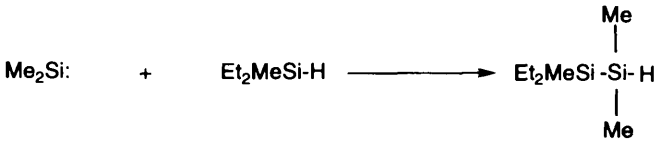
$$Me_2SiCl_2 \xrightarrow[M\,=\,Na\text{-}K,\ Na,\ Li]{M} Me_2Si\!: \qquad (8.27)$$

It is also prepared by a decomposition reaction with heat or light. For example, the silylenes are obtained by light irradiation of the cyclic compounds [9,12]. In contrast, silylenes form cyclic compounds as described below,

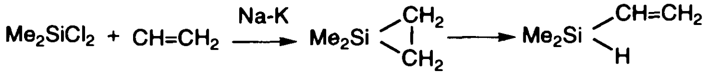


Me₂Si: (8.28)

In organosilylenes, insertion, addition, cyclization and polymerization proceed. Insertion and cyclization are shown in eqs. (8.29) and (8.30), respectively [9,12,14].

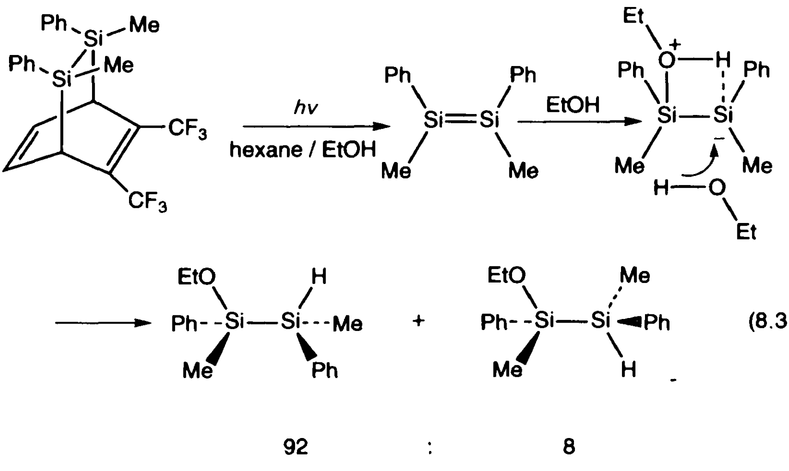


$$\mathrm{Me_2Si{:}} \quad + \quad \mathrm{Et_2MeSi\text{-}H} \longrightarrow \mathrm{Et_2MeSi\text{-}\underset{Me}{\overset{Me}{Si}}\text{-}H} \qquad (8.29)$$



(8.30)

The bond length of a double bond of disilylene ($R_2Si{=}SiR_2$), bonded with two moles of silylenes, is 2.116 Å, and it is longer than that of a carbon–carbon double bond (1.315 Å). Therefore it is liable since the π bond energy is small. However, Diels–Adler type addition products obtained by 1,4-addition with benzene derivatives are stable and the handling is easy. The silylene is reproduced by light irradiation of this addition product and, for example, the reaction with alcohol proceeds stereoselectively as shown in eq. (8.31) [19]. When the silylenes react with benzene or naphthalene, [1 + 2] cycloadditions proceed. The example with naphthalene is shown in eq. (8.32) [19–22].

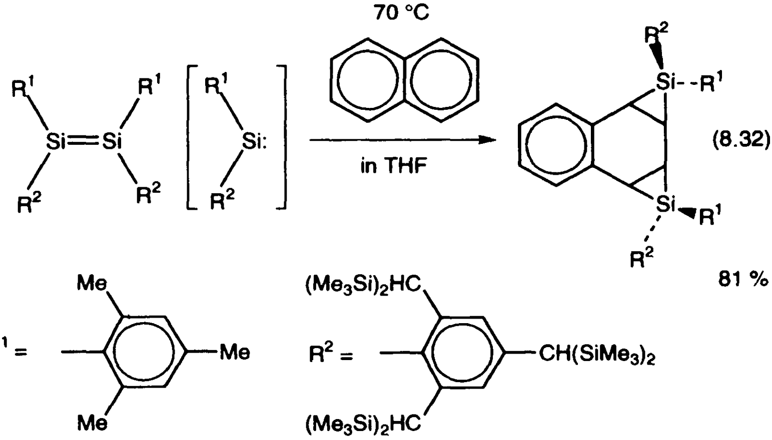


(8.31)

8.4.4 REARRANGEMENTS

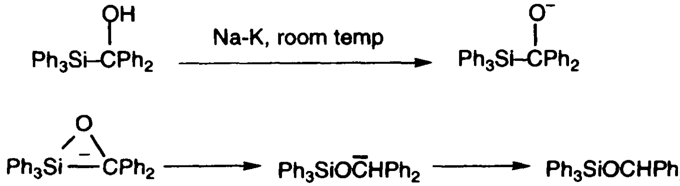
As for the rearrangements of organosilicon compounds, there are anionic rearrangements, rearrangements of methylpolysilanes, radical rearrangements, α-carbonium ion rearrangements, etc. [14].

The silicon atom has a strong affinity to oxygen and the Si–O bond is a strong bond. Hence, the formation reactions of Si–O bonds tend to proceed easily. For



(8.32)

example, when a small amount of Na–K alloy is added to an ether solution of triphenylsilyldiphenylcarbinol, the rearrangement product, silylether, is easily obtained at room temperatures as shown in eq. (8.33) [14,23]. Bases such as triethylamine are available as the catalyst. This rearrangement is the reverse reaction of the Wittig rearrangement which is an anionic rearrangement. But, with organolithium compounds such as *t*-butyllithium as a catalyst, the rearrangement from silylether to silylcarbinol is similar to the Wittig rearrangement [14,24].

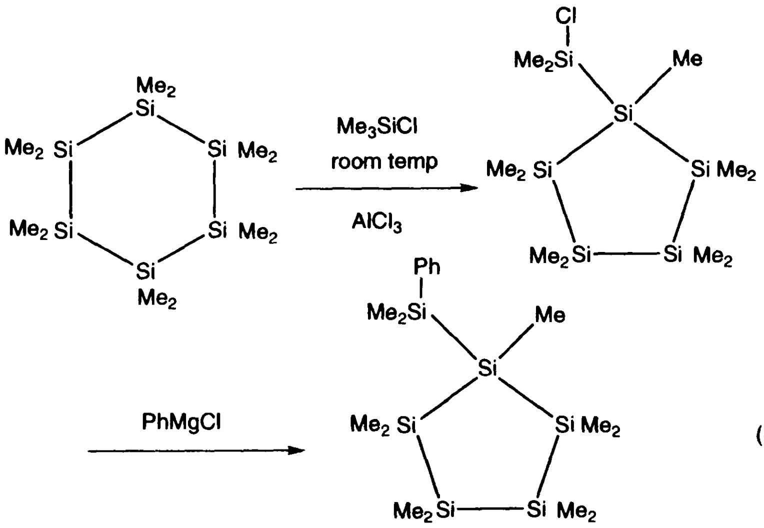


(8.33)

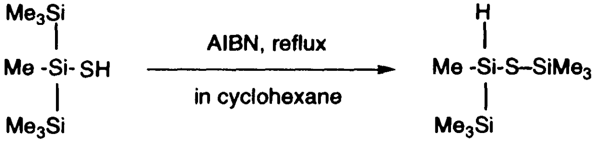
The skeleton rearrangement of methylpolysilanes was found by Kumada in 1969, in which the rearrangement is carried out at room temperatures by the reaction of cyclohexasilane with trimethylchlorosilane in the presence of aluminum chloride catalyst and the monochloro derivative is obtained and the arylation with Grignard reagents proceeds as shown in eq. (8.34) [25].

Disilanes or trisilanes are heated at high temperatures, or heated in the presence of radical initiator such as AIBN, and the radical rearrangement proceeds. For example, heptamethyltrisilane-2-thiol is heated in cyclohexane in the presence of AIBN and then immediately and quantitatively a rearrangement product is obtained as shown in eq. (8.35) [26].

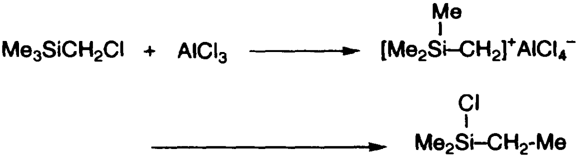
Chloromethyltrimethylsilane reacts with aluminum chloride to give an α-carbonium ion and the Wagner–Meewein type rearrangement proceeds easily as shown in eq. (8.36). Similarly, in disilane, the rearrangement proceeds quantitatively as shown in eq. (8.37) [14,27,28].



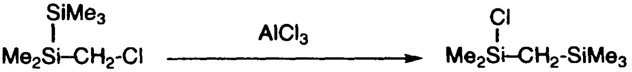
(8.34)



$$\mathrm{Me-\underset{Me_3Si}{\overset{Me_3Si}{Si}}-SH \xrightarrow[\text{in cyclohexane}]{\text{AIBN, reflux}} Me-\underset{Me_3Si}{\overset{H}{Si}}-S-SiMe_3} \tag{8.35}$$



$$\mathrm{Me_3SiCH_2Cl + AlCl_3 \longrightarrow [Me_2\overset{Me}{Si}-CH_2]^+AlCl_4^- \longrightarrow Me_2\overset{Cl}{Si}-CH_2-Me} \tag{8.36}$$



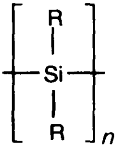
$$\mathrm{Me_2\overset{SiMe_3}{Si}-CH_2-Cl \xrightarrow{AlCl_3} Me_2\overset{Cl}{Si}-CH_2-SiMe_3} \tag{8.37}$$

8.4.5 POLYMERIZATIONS

Organosilicon compounds give various kinds of polymers by polymerization reactions as described below. This section shows only the representative type of polymers and ring opening reactions discovered recently [14,29,30].

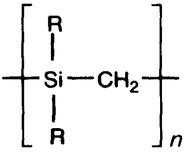
The polymers which are prepared by the polymerization of organosilicon compounds are classified into two types. One type is organosilicon polymers having a silicon atom in the principal chain. The other type is an organosilicon polymer having a silicon atom in the side chain. The polymer in which atoms of the principal chain are all silicon atoms is a polysilane. The polymers in which the principal chain is composed of silicon and carbon atoms are called polysilylmethylenes. The polymers in which the principal chain is composed of silicon and hetero atoms are called polysiloxanes or polysilazanes. The polymers in which the side chains contain a silicon atom are poly(trimethylvinylsilane) and poly(p-trimethylsilylstyrene), etc. [14].

polysilanes



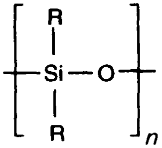
$$\left[\begin{array}{c} R \\ | \\ -Si- \\ | \\ R \end{array}\right]_n$$

polysilylmethylenes



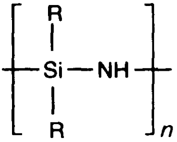
$$\left[\begin{array}{cc} R & \\ | & \\ -Si & -CH_2- \\ | & \\ R & \end{array}\right]_n$$

polysiloxanes



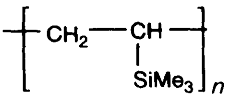
$$\left[\begin{array}{cc} R & \\ | & \\ -Si & -O- \\ | & \\ R & \end{array}\right]_n$$

polysilazanes



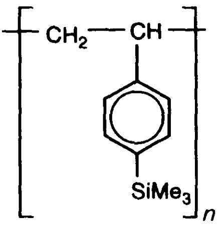
$$\left[\begin{array}{cc} R & \\ | & \\ -Si & -NH- \\ | & \\ R & \end{array}\right]_n$$

polytrimethylvinylsilane

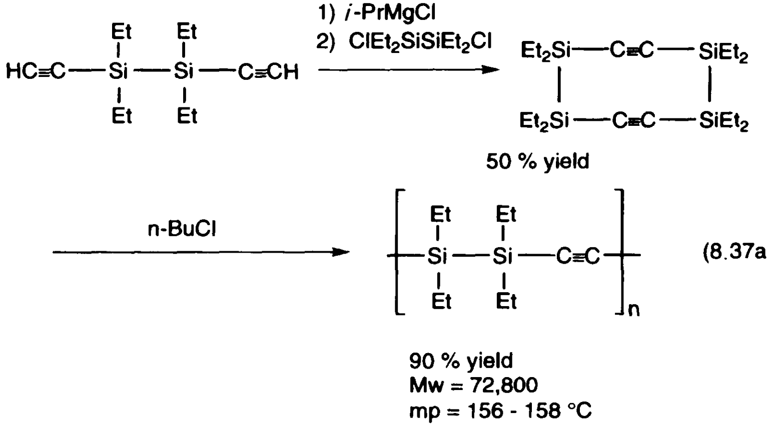


$$\left[\begin{array}{cc} -CH_2 & -CH- \\ & | \\ & SiMe_3 \end{array}\right]_n$$

poly-p-trimethylsilylstyrene



An anionic ring opening reaction is shown in eq. (8.37a). This is the synthetic example of a polymer in which the principal chain contains a silicon atom produced by a ring opening polymerization [30a,30b].



(8.37a)

8.5 CHARACTERISTICS OF ORGANOSILICON COMPOUNDS

Silicone, which is the representative industrial product of organosilicon compounds, has many characteristic properties such as heat resistance, weather resistance, cold resistance, electric insulating, water repellency, antifoaming properties, mold release properties, lubricating properties, etc. Hence the silicones are used in various industrial fields [31].

The characteristics of silicones are caused mainly by the following two properties.

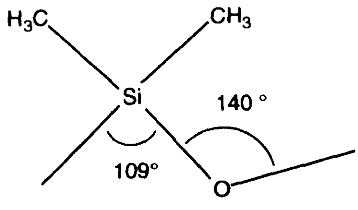
(1) Strong Si–O bond
(2) Small intermolecular force

The bond energy strengths are shown in Table 8.2 [31]. In the Si–O bond in the principal chain of silicones, the difference in electronegativity of Si and O (electronegativity: Si = 1.74; O = 3.50) is large, i.e., the Si–O bond is almost an ionic bond and is stabilized energetically. Thus it forms a strong bond. The Si–O bond has a similar bond to that in rocks such as silicas. Therefore, the Si–O bond has a high heat resistance and oxidation resistance. On the other hand, the Si–C bond energy of the side chain is smaller than the C–C bonds or C–H bonds as shown in Table 8.2. But, in fact the Si–C bond is more stable than C–C and C–H bonds because $-CH_2-CH_2-$ bonds form unstable $-CH=CH-$ by a dehydrogenation reaction at high temperatures, and the decomposition extends from this site as a

Table 8.2 Bond energies [31]

	Bond energy (kcal/mol (kJ/mol))	
Element	C	Si
C	83.2 (349)	58–80 (240–340)
Si	58–80 (240–340)	45.0 (189)
H	98.8 (414)	72.6 (304)
O	83.2 (349)	101 (423)

starting point. In contrast, the Si=C bond does not tend to form since Si does not form sp^2 hybridized orbitals in the case of the Si−C bond. Further, the Si−H bond is more stable than the C−H bond in hydrocarbons, because the ionic property of $\overset{\delta-}{C}-\overset{\delta+}{H}$ decreases because of the effect of the ionic structure of the Si−O bond in the principal chain and it is also not liable for an attack with other molecules [31]. Hence, silicones show high heat resistance and high oxidation resistance because of the strong Si−O bond being the first characteristic property and the chemical stability of Si−CH_3 also caused by the first characteristic property. Moreover, silicones show water repellent, water resistant qualities, moisture resistance and weather resistance because the SiC−H bond has small ionic properties [31]. Another characteristic of silicone is a small intermolecular force that is caused by a high polarizable state, that is, the state in between covalent bonds and ionic bonds because of a large difference in the electronegativities of Si and O in the Si−O bond. As the valence angle of a pure covalent bond is fixed, a large energy is required even if the change in this angle is slight. But since the bond is highly polarizable, the angle is able to be changed with only a small amount of energy. Hence, in the polymethylsiloxane, the $Si(CH_3)_2$ unit thermally vibrates through a relatively large degree, and it keeps its position away from the adjacent molecules. Eventually, the average intermolecular distance becomes large. As the intermolecular force abruptly decreases with increasing intermolecular distance, the intermolecular force of polysiloxanes becomes very small. As described above, the polarizability of the SiC−H bond is small and it further decreases the intermolecular force [31].



By the small intermolecular force of the second characteristic property of silicones, the solidification point becomes lower, and the silicones have high cold resistance. Besides, a small intermolecular force means that the distance between one molecule and the other molecule is large. Therefore gas permeabilities such as that of oxygen of the silicones are large and the compressibilities of the silicones are high. Furthermore, by both the property of small intermolecular force and small polarity, the silicones show a high water repellency, mold release and lubricating properties [31]. Foam is that liquid state which encloses gas and forms a globular shape by its surface tension. If a substance having a small surface tension such as silicones adheres to foam, the surface tension decreases locally. Since the surrounding substances have large surface tension and pull mutually, the foam is broken just as if a wedge was driven into it. Hence silicones act as antifoaming agents [31].

Silicones are more flame resistant than ordinary polymers composed of C, H and O, since silicones have Si, a noncombustible component. Furthermore, silicones are suitable for materials in foods and medical treatment since they are physiologically and chemically inactive [31].

As mentioned above, silicones are widely used since they have various remarkable properties. Organosilicon compounds other than silicones are used not so much, but their applications are described in the next section.

8.6 APPLICATIONS OF ORGANOSILICON COMPOUNDS

The most commonly used organosilicon compounds are silicones as described above. The others are chlorosilanes, alkoxysilanes, silazanes, fluoroalkylsilanes and polysilanes as shown in Table 8.3 [31].

8.6.1 SILICONES

Silicones are polymeric compounds containing a siloxane bond (Si–O) and there are three forms of silicones, i.e., oils, rubbers, and resins as shown in Table 8.4 [31]. In Japan the ratio of consumption of these three forms of silicones is 35 : 55 : 10 where the rubber are used most, the second most used is oil and the resins occupy only 10 %. In the consumption pattern in the United States and Europe, the oils are used most (especially in the United States, where the oils are used as much as 65–70 %), the rubbers are 25–30 % and resins are only 7 %.

8.6.1.1 Silicone Oils

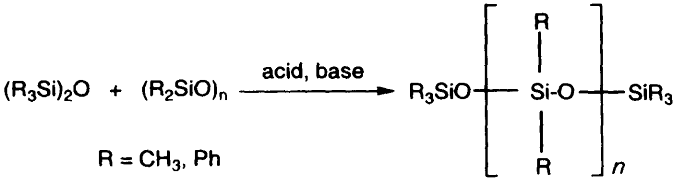
Silicone oils are linear polysiloxanes obtained by the following two-step process. The first is that siloxanes are prepared by hydrolysis of trimethylchlorosilane or dimethyldichlorosilane. The second is a polymerization of siloxanes with acid or alkali as shown in eqs. (8.38)–(8.40) [32,33].

Table 8.3 Uses of organosilicon compounds [31]

Organosilicon compounds	Silicones $-\!\!\left[\overset{|}{\underset{|}{\mathrm{Si}}}\text{-O}\right]_n\!\!-$	
	Chlorosilanes $R^1_m R^2_n SiCl_{4-(m+n)}$ R^1, R^2 = H, Me, Bu, Ph, $C_{18}H_{37}$, etc.	Raw materials for silicones Silylating agents Raw materials for SiC Treatments for filler of liquid chromatography
	Alkoxysilanes $-\overset{|}{\underset{|}{\mathrm{Si}}}\text{-OR}$ R = Me, Et, etc.	Silane coupling agents Silicone hard coat Catalysts for olefin polymerization Waterproofing materials Treatments for filler of liquid chromatography
	Silazanes $-\overset{|}{\underset{|}{\mathrm{Si}}}\text{-N-}$	Silylating agents Surface treatments for silicon wafer Raw material for Si_3N_4
	Fluoroalkylsilanes $CF_3(CF_2)_nCH_2CH_2SiXY_2$ X,Y = Me, OMe n = 0, 5 or 7	Processing materials for strainproof Orientation improvers for liquid crystal Treatments for lenses with antireflection
	Polysilanes $-\overset{|}{\underset{|}{\mathrm{Si}}}-\overset{|}{\underset{|}{\mathrm{Si}}}-$	Photoresist polymers Raw materials for SiC Electroconductive materials

$$ZR_3SiCl + H_2O \longrightarrow (R_3Si)_2O \qquad (8.38)$$

$$R_2SiCl_2 + H_2O \longrightarrow (R_2SiO)_n \qquad (8.39)$$



$$(R_3Si)_2O + (R_2SiO)_n \xrightarrow{\text{acid, base}} R_3SiO\left[\begin{array}{c}R\\ |\\ \text{Si-O}\\ |\\ R\end{array}\right]_n SiR_3 \qquad (8.40)$$

R = CH_3, Ph

Table 8.4 Uses of silicones [31]

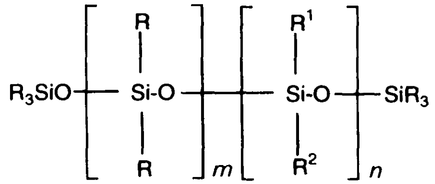
Silicone	Silicone oils (Silicone pastes) (Silicone fats)	Heat exchangers
		Foam stabilizers
		Mold release agents, Removers
		Water-repellent agents
		Antifoaming agents
		Lubricants
		Insulating oils
		Vibration isolating oils (high compressibility)
		Hydraulic oils (e.g., clutch oils)
		Additives for plastics, paints, toiletries, etc.
		Shock-absorbing oils
		Textile treatments (hand improvers, smoothing agents, repellents, etc.)
	Silicone rubber	Heat-resistant rubber (wire coating, etc.)
		High strength rubber
		Weather-resistant rubber
		Cold-resistant rubber
		Chemical-resistant rubber (resistance to oils, solvents, ozone, etc.)
		Fatigue-resistant rubber (packings, belts, etc.)
		Gas-permeable rubber (contact lenses, artificial lungs, artificial skin, etc.)
		Fire resistant rubber
		Electroconductive rubber
		Medical rubber (physiological inertness, neutral, hydrophobic and chemical resistance)
	Silicone resins	Heat-resistant resins (vanishes)
		Weather-resistant resins (vanishes)
		Moisture, weathering resistant resins (vanishes)
		Chemical-resistant resins (lining materials, etc.)
		Abrasion-resistant resins (coating materials)
		Insulating resins (sealing compounds)
		Fire-resistant resins (vanishes)
		Pressure-sensitive adhesive resins
		Spherical powders (improvers to blocking and sliding properties for films)

The degree of polymerization of polysiloxane is determined by the molar ratio of $(R_3Si)_2O$ and $(R_2SiO)_n$. In the silicon oils, n is 0 to several hundred, and the viscosity is 0.65 cSt (centistokes) to 10^6 cSt [31,34].

Methylchlorosilanes are usually used as raw materials of silicone oils, but the combination with other silanes such as phenylchlorosilanes gives various kinds of silicone oils.

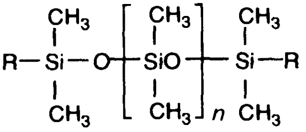
In the above reaction, if R, R^1 and R^2 are all CH_3, the product is a dimethylsilicone oil. If R is CH_3, and R^1 and R^2 are Ph, the product is a methylphenylsilicone oil.

$$(R_3Si)_2O + (R_2SiO)_m + (R^1R^2SiO)_n \longrightarrow$$



$$R_3SiO\left[\begin{array}{c} R \\ | \\ Si\text{-}O \\ | \\ R \end{array}\right]_m\left[\begin{array}{c} R^1 \\ | \\ Si\text{-}O \\ | \\ R^2 \end{array}\right]_n SiR_3 \qquad (8.41)$$

If the ratio of the phenyl group is large, the polymer shows high heat resistance. If the ratio is small, the polymer has a high cold resistance. If R and R^1 are CH_3 and R^2 is H, the polymer is called methylhydrogen silicone oil, and since the silicone oil is reactive they are used in water repellant treatment for clothes, etc. [31]. If R^2 is another specific group besides H, CH_3 and Ph, or if the R of the following silicone polymers is a functional group, the polymers are called degenerated silicone oils [31].



$$R-\begin{array}{c} CH_3 \\ | \\ Si \\ | \\ CH_3 \end{array}-O\left[\begin{array}{c} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{array}\right]_n\begin{array}{c} CH_3 \\ | \\ Si \\ | \\ CH_3 \end{array}-R$$

If R^2 is a long alkyl chain or a higher fatty acid residue, the polymers are called alkyl degenerated silicone oils or higher fatty acid degenerated silicone oils, respectively. These silicone oils have a high lubricant property and a high dissolution property.

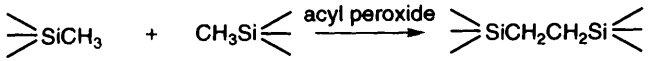
If R^2 is polyoxyalkylene, hydroxyalkyl, aminoalkyl, epoxy, etc., these polymers are called polyoxyalkylene degenerated silicone oils, alcohol degenerated silicone oils, amino degenerated silicone oils, epoxy degenerated silicone oils, etc., respectively. As these silicone oils have reactive functional groups, they are able to react with organic substances, resins and fibers, etc. Therefore they are available as modifying agents which give a mold releasing property and flexibility, etc. [31].

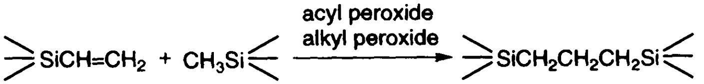
Recently the competition in research and development into these polymeric modifying agents is keen and many patents are becoming available to the public.

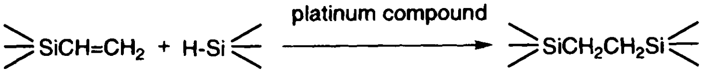
The solidified or semisolidified silicones are made by adding fillers to the silicone oils. They are then called silicone fats or silicone pastes. There is no clear difference between silicone fats and silicone pastes. However, those called silicone fats are used mainly for lubricants as metal soap type fillers. They are called silicone pastes when they are used as non-metal soap type fillers. The silicone pastes lack lubricating properties and they are used mainly as electric insulators and waterproof seals for electric parts, electronic parts, machinery and tools [31,35]. The silicone oils used are of various kinds as shown in Table 8.4.

8.6.1.2 Silicone Rubbers

Silicone rubbers are prepared by the vulcanization of linear high polymeric polysiloxanes (raw rubbers) and by partial cross-linking they become rubber-like. There are two kinds of silicone rubbers, i.e., one is a millable type silicone rubber and the other is a liquid type silicone rubber. Formerly, silicone rubbers were classified as hot vulcanizable in which they become an elastic gum on heating, and a cold vulcanizable (or room temperature vulcanizable (RTV)) in which they become an elastic gum by leaving them at room temperatures. However, RTV silicone rubbers, as described below, are prepared by two reactions of an addition type and condensation type. But, recently, in the addition type, the silicone rubbers which are prepared by vulcanization at a similar temperature to the hot vulcanization type were found. Therefore, the silicon rubbers could no longer be classified by vulcanization temperatures. Hence, now the silicone rubbers are classified by the polymerization type of the raw rubbers or by the viscosity. Then they are called millable type silicon rubbers or liquid type silicone rubbers [31,34,35]. In the millable type silicone rubbers, high molecular weight polysiloxanes (5000–10000 siloxy units, semisolid), are prepared by the reaction shown in eq. (8.41). They are used as the raw material, the peroxides or platinum compounds (chloroplatinic acid or its derivatives) are used as vulcanization agents, and the rubbers are prepared by a radical cross-linking reaction (eq. (8.42)) or by addition reactions (eqs. (8.43) and (8.44)) after vulcanizations [31,34,35].

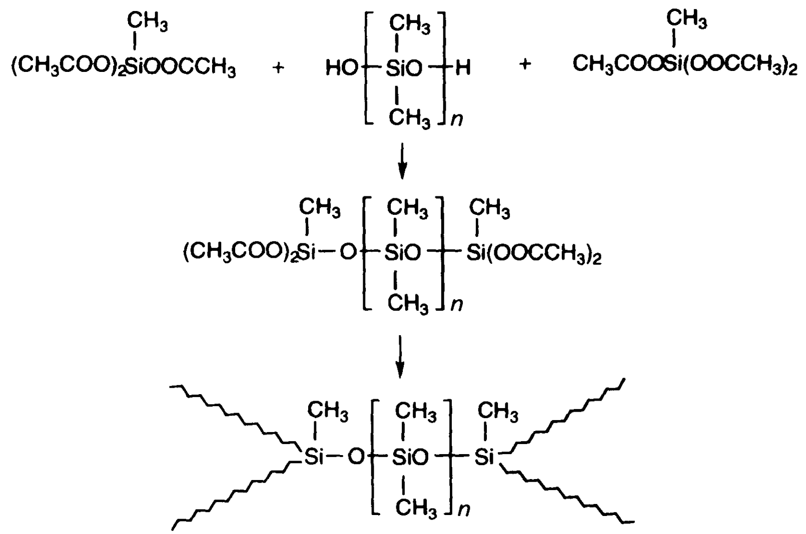

$$>SiCH_3 + CH_3Si< \xrightarrow{\text{acyl peroxide}} >SiCH_2CH_2Si<$$
(8.42)


$$>SiCH{=}CH_2 + CH_3Si< \xrightarrow[\text{alkyl peroxide}]{\text{acyl peroxide}} >SiCH_2CH_2CH_2Si<$$
(8.43)


$$>SiCH{=}CH_2 + H\text{-}Si< \xrightarrow{\text{platinum compound}} >SiCH_2CH_2Si<$$
(8.44)

On the other hand, liquid silicone rubbers are liquid or paste-type polysiloxanes prepared by using the raw siloxanes having functional groups which are liable to cross-linking at the terminal position. Liquid silicon rubbers are prepared by the cross-linking of these siloxanes. There are two cross-linking types of condensation and addition as follows.

(i) Condensations. Condensation type silicone rubbers are cross-linked polysiloxanes prepared by the condensation of polysiloxanes having a hydroxy group at the terminal position. For example, the cross-linking reaction is carried out using an



Scheme 8.1 Preparation of liquid silicone rubbers by condensation reaction [31,34].

acetate as the cross-linking agent as shown in Scheme 8.1. The other cross-linking agents are alkoxide ($MeSi(OMe)_3$), oxime ($MeSi(O-N{=}CMeEt)_3$), amide ($Me(CH_2{=}CH)Si(-NEtCOMe)_2$), etc. [31,34].

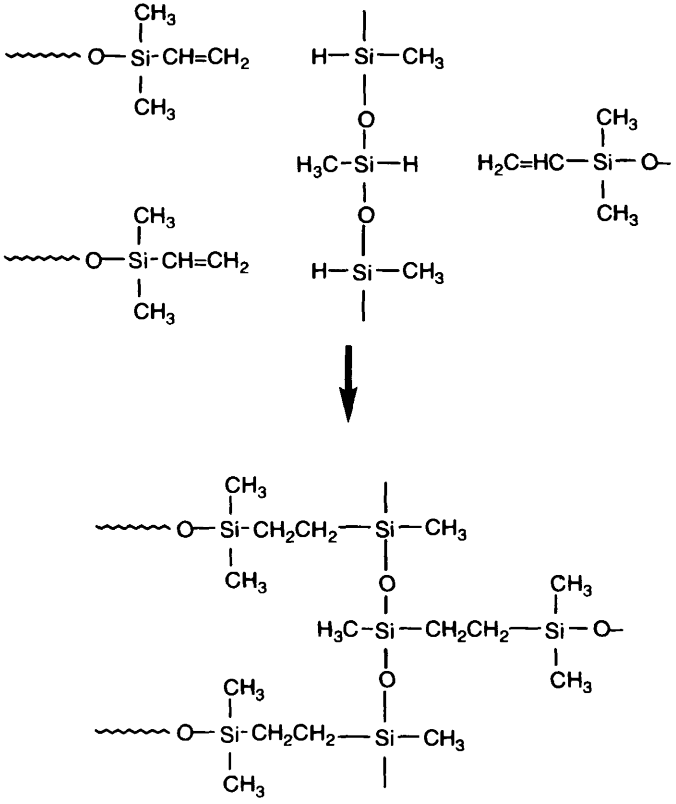
(ii) Addition types. In the case when the terminal group of a polysiloxane is a vinyl group, and polysiloxanes having SiH are used as the cross-linking agent, the cross-linking reaction is carried out by the addition reaction with a platinum catalyst as shown in Scheme 8.2 [31,34].

The other vulcanization of liquid silicones is a radical reaction with UV irradiation at room temperatures. As silicone rubbers are anti-thrombotic, non-toxic, hydrophobic, not reactive with living tissue and chemically stable compared with the other polymers, they are used for parts dealing with blood and other medical materials. The silicone rubbers are used in various parts having a high heat resistance and a high fatigue resistance by adding electrically conductive materials such as carbon black. The uses of silicone rubbers are shown in Table 8.4.

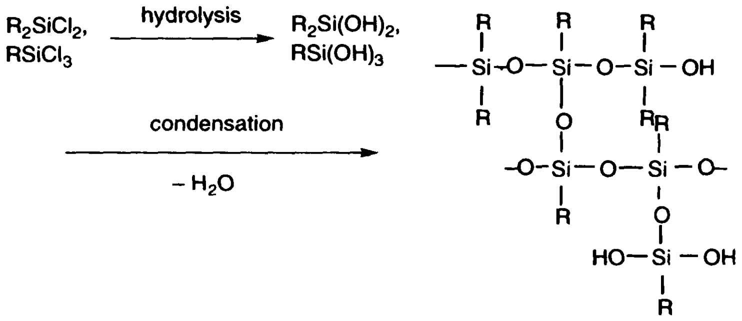
8.6.1.3 Silicone Resins

Silicone resins are prepared by hydrolysis of chlorosilane to give the silanol, followed by condensation as shown in Scheme 8.3, and they are three-dimensional cross-linked resinoid solids of polysiloxanes.

On the other hand, the chlorosilanes react with methyl alcohol or ethyl alcohol to give the mixture of alkoxides ($R_2Si(OR^1)_2$ and $RSi(OR^1)_3$), and the silicone resins are also prepared by condensation of the mixture. The temperature range of the condensation is 200–250°C. The condensation becomes fast with catalysts such as organic acid metal salts (e.g., Pb, Zn, Fe and Sn) or amines.



Scheme 8.2 Preparation of liquid silicone rubbers by addition reaction [31,34].



Scheme 8.3 Preparation of silicone resins [31,34].

The silicone resins are used as silicone varnishes, sealing compounds and spherical powders as shown in Table 8-4.

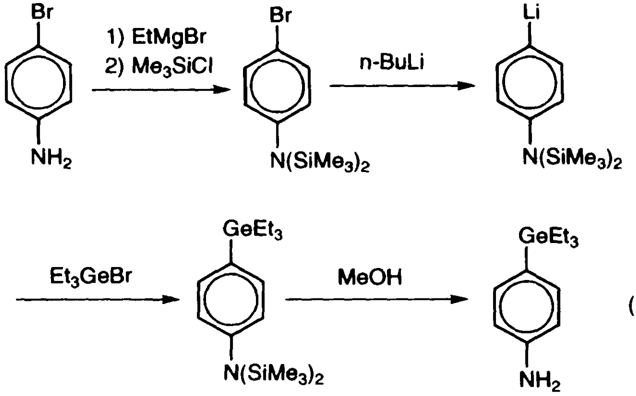
8.6.2 CHLOROSILANES

Chlorosilanes are prepared by the reaction of alkyl halides with metal silicon in the presence of copper catalyst. This direct reaction was published in 1945. However, its discovery was five years earlier, in May 1940 and the half-century was in 1990 [2,11,12,36–40].

$$2RCl \quad + \quad Si \quad \xrightarrow[\substack{250-300\ ^\circ C\ (R = Me) \\ 400-500\ ^\circ C\ (R = Ph)}]{Cu} \quad R_2SnCl_2 \qquad (8.45)$$

If the direct reaction is carried out at the lowest temperature at which the reaction proceeds, dichlorosilanes, R_2SiCl_2, are the major products and the other products are R_3SiCl and $RSiCl_3$, etc. The chlorosilanes (R_nSiCl_{4-n}, $n = 1$–3, R = Me, Ph) are used not only as the raw materials of silicones but also as the starting materials of various kinds of organosilicon compounds such as alkoxysilanes, silazanes, fluoroalkylsilanes and polysilanes as shown in Table 8.3 [31].

The silylating agents are the reagents which substitute an active hydrogen such as $-OH$, $-NH_2$ and $-COOH$ with silyl groups (R_3Si-). These reagents are used, at first for gas chromatographic analysis by which slightly volatile compounds such as saccharides and amino acids are converted to volatile compounds. Now they are widely used for protecting the active groups in the syntheses of pharmaceuticals. The silylating agents are not only chlorosilanes (Me_3SiCl, *t*-$BuMe_2SiCl$, etc.) but also aminosilanes (Me_3SiNMe_2, Me_3SiNEt_2, etc.) [31]. For example, as the amino group of *p*-bromoaniline is highly reactive, *n*-BuLi cannot react directly with Br in *p*-bromoaniline. Thus, first, the amino group is protected by trimethylsilane, the object group is substituted, and finally alcohol reacts to give the amino derivatives by removing the protecting group [41].



(8.46)

The order of the reactivity of active hydrogen is generally as follows [31]:

$$\mathrm{ROH > ArOH > COOH > NH > CONH > SH}$$

Recently, SiC, which is produced from chlorosilanes, is the most important ceramic of the silicon-type ceramics. SiC is described in detail in the section on polysilanes and the other silicone ceramics are Si–C–O, Si_3N_4, Si–N–C and Si–C–Ti–O, etc. [42–44].

The other uses of chlorosilanes are as treatment agents for packing materials for liquid chromatographic analysis of pharmaceuticals and proteins [31].

8.6.3 ALKOXYSILANES

Alkoxysilanes are easily prepared by the reaction of chlorosilanes with alcohols. When alkoxysilanes contact inorganic materials, they are hydrolyzed by the moisture absorbed on the surface to give the silanol ($R_nSi(OH)_{4-n}$). Further, the silanols form the Si–O–M bond to the surface of the inorganic materials (M–OH).

$$R_nSiCl_{4-n} \quad + \quad (4-n)\,R^1OH \longrightarrow R_nSi(OR^1)_{4-n} \qquad (8.47)$$

Hence, they are able to bond to inorganic materials. In this manner, as the alkoxysilanes show a strong adhesion between organic materials and inorganic materials, they are called silane coupling agents [31]. The general formula of silane coupling agents is $Y\text{-}(CH_2)_nSi(OR)_3$ ($Y =$ vinyl, acyl, epoxy, amino, mercapto and halogen group, $n = 0$, 1–3, $R = Me$, Et). They bond to organic materials with the functional group Y. On the other hand, the alkoxy group (OR) is hydrolyzed to the silanol and bonds to inorganic materials. The silane coupling agents, are, for example, $CH_2{=}CHSi(OEt)_3$, $Cl(CH_2)_3Si(OMe)_3$, $H_2N(CH_2)_3Si(OMe)_3$, and  $\underset{\diagdown O \diagup}{CH_2{-}CH}CH_2O(CH_2)_3Si(OMe)_3$, $HS(CH_2)_3Si(OMe)_3$ [31,34]. The silane coupling agents at first were used as the surface treatment agent for glass fibers, and then for resin concretes, shell molds, and adhesive paints and primers. Silane coupling agents are used in composite materials comprising inorganic and organic materials. The mixture of silica and $MeSi(OMe)_3$, $Si(OMe)_4$ or $MeSi(OMe)_3$ is applied on the surface of plastics. They are then hydrolyzed and cured by condensation, form a glassy film and become like a ceramic coating. Therefore, the surfaces are improved not only with abrasion resistance but also with moisture, chemicals and solvent resistance. Thus, they are used as hard coating agents [31,34].

As alkoxysilanes have a small intermolecular force and a small surface tension, they percolate through a capillary wall and form a strong waterproof layer, and they protect the deterioration of buildings caused by water adsorption, frost damage, injury from salt, UV, etc. Therefore, they are used as waterproof agents [31,34].

8.6.4 SILAZANES

The representative organosilicon compounds having an Si–N bond are silazanes. The silazanes are usually prepared by the reaction of chlorosilanes with ammonia. For example, trimethylchlorosilane reacts with ammonia to give hexamethyldisilazane. Dimethyldichlorosilane reacts with ammonia to give a mixture of cyclic hexamethylcyclotrisilazane and octamethylcyclotetrasilazane [31].

$$2Me_3SiCl + 3NH_3 \longrightarrow Me_3SiNHSiMe_3 + 2NH_4Cl \quad (8.48)$$

$$Me_2SiCl_2 + 2NH_3 \longrightarrow (Me_2SiNH)_3 + (Me_2SiNH)_4 \quad (8.49)$$

The silazanes having a Si–N bond have a similar high reactivity as chlorosilanes having a Si–Cl bond. Thus, they are easily hydrolyzed or alcoholized to give silanols or alkoxysilanes. Hence, the silazanes are also used as silylating agents similar to the chlorosilanes described in the previous section. The silazanes are used as the raw materials for ceramics (Si_3N_4). Their other use is in surface treatments for silicon wafers to improve their wetting properties and adhesion properties [31].

$$Me_3SiNHSiMe_3 + 2H_2O \longrightarrow 2Me_3SiOH + NH_3 \quad (8.50)$$

$$Me_3SiNHSiMe_3 + 2ROH \longrightarrow 2Me_3SiOR + NH_3 \quad (8.51)$$

8.6.5 FLUOROALKYLSILANES

Fluororesins are of low reactivity, chemically stable, water repellant and oil repellant compared with hydrocarbon-type resins. Therefore, the bonding strength (adhesion) to the base materials of fluoroalkyl compounds is weak. But the compounds in which the fluoroalkyls bond to alkoxysilanes or chlorosilanes show strong bonding strengths compared to inorganic materials as described above, and they are used as processing materials for stainproofing agents. The representative compounds are as follows [31].

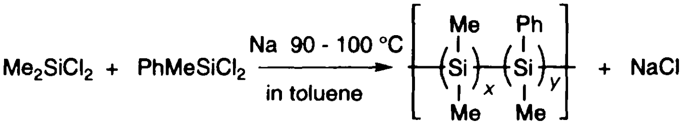
$$CF_3(CH_2)_nCH_2CH_2Si(OMe)_3 \qquad n = 0, 5, 7$$

$$CF_3(CH_2)_nCH_2CH_2SiCl_3 \qquad n = 0, 5, 7$$

If the surface of a glass cell is treated with fluoroalkylsilanes, the orientation for a liquid crystal is improved. If the surface of plastic lenses is treated with them, the refractive index of the surface is lowered. The treatment also gives the lenses a low reflective power due to the difference of the relative refractive indices between base plastics and the surface coating [31].

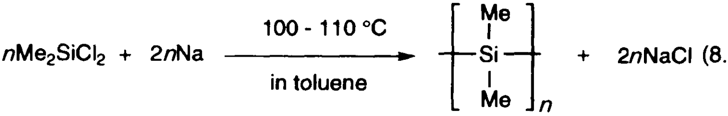
8.6.6 POLYSILANES

Polysilanes [45–59] are compounds having Si–Si bonds. The high polymeric polysilanes have increased crystallinity and become insoluble and infusible materials. Hence, polysilanes have not been found to have such useful properties as polysiloxanes. But, in 1980, Robert West obtained high molecular weight polysilanes which are able to be spun and to be formed as a film by copolymerizing with Me_2SiCl_2 and $PhMeSiCl_2$, and these polysilanes got into the spotlight as industrial materials since it was found that they show semiconductor properties.



$$Me_2SiCl_2 + PhMeSiCl_2 \xrightarrow[\text{in toluene}]{\text{Na } 90-100\,^\circ C} \left[(\overset{Me}{\underset{Me}{Si}})_x (\overset{Ph}{\underset{Me}{Si}})_y \right] + NaCl \quad (8.52)$$

Polysilanes have been investigated as the raw materials of new ceramics, photoresist polymers for high resolution lithography, semiconductors, electroconductive polymers, etc. [46]. Polydimethylsilane is prepared by adding dichlorosilane to the dispersed minute particles of sodium in toluene solution.



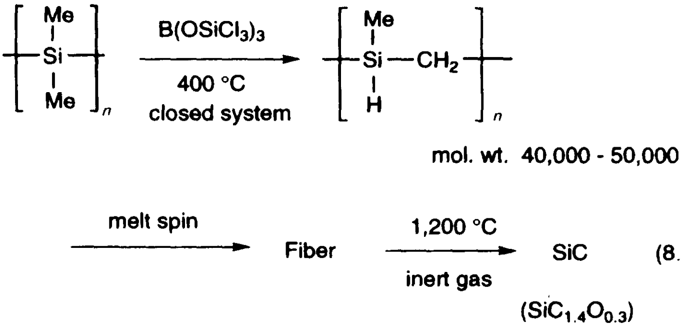
$$nMe_2SiCl_2 + 2nNa \xrightarrow[\text{in toluene}]{100-110\,^\circ C} \left[\overset{Me}{\underset{Me}{Si}} \right]_n + 2nNaCl \quad (8.53)$$

mol. wt. 1,500 - 2,000, mp ≈ 280°C

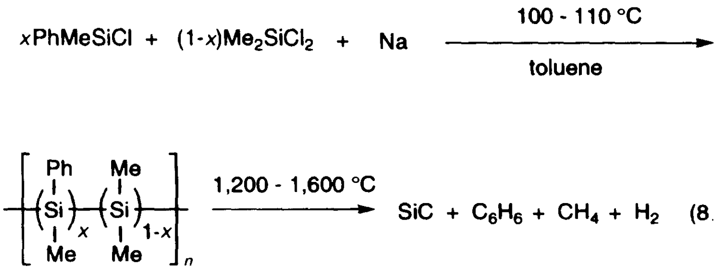
If the reaction temperature is low, it tends to give cyclic polysilanes (mainly the six membered ring shown in eq. (8.34), and the other products are four membered ring or eight membered ring compounds). The linear polysilanes (eq. (8.53)) are insoluble white solids. If these polysilanes are heated at 400°C in the presence of $B(OSiCl_3)_3$ in a sealed system, the polymers are rearranged to form polycarbosilanes ($(-SiMe(H)-CH_2-)_n$) as a soluble solid.

The carbosilanes are melt spun, heated at 200°C in air for the protection from fusing, and finally SiC fibers are obtained by releasing methyl radical and hydrogen with heating at 1200°C in an inert gas atmosphere. The SiC fibers are sold with the trade name Nicalon. The tensile strength is 300 kg/mm^2 and it is used as a high strength fiber which can stand heating at 1000°C or higher [60,61].

Polysilastyrene is also prepared in a way similar to polysilane as shown in eq. (8.52). Actually the polysilastyrene having $x = 0.5–0.6$, due to consideration of its yield and the price of its raw materials, is prepared. The molecular weight is around 30000–60000. The SiC is produced by releasing organic gas with calcination of polysilastyrene at 1200–1600°C under an argon atmosphere [61].



(8.54)



(8.55)

Polysilastyrene absorbed $\leq 350\,\mathrm{nm}$ UV radiation and its molecular weight easily decreases by breaking of the Si–Si bonds. Therefore, the polysilastyrene can be used as a photoresist. Other various kinds of polysilanes have been developed, as shown in Table 8.8 [61].

The electric conductivities of polysilanes are $< 1 \times 10^{-12}\,\Omega\mathrm{cm}$ and it is almost an insulator, but, if they are doped with an electron acceptor such as AsF_5, for example, the electric conductivity of $[(Me_2Si)_{0.5}(PhMeSi)_{1.0}]_n \cdot AsF_5$ becomes $2 \times 10^{-1}\,\Omega\mathrm{cm}^{-1}$, and the electric conductivities are drastically increased as shown in Table 8.5 [49].

Table 8.5 Conductivity of polysilanes doped with oxidants [49]

Polymer†	Dopant	Pressure (Torr)	Conductivity ($\Omega \cdot \mathrm{cm}^{-1}$)
$[(Me_2Si)_{1.0}(PhMeSi)_{1.0}]_n$	none		$< 1 \times 10^{-12}$
$[(Me_2Si)_{1.0}(PhMeSi)_{1.0}]_n$	AsF_5	15	1.5×10^{-6}
$[(Me_2Si)_{0.5}(PhMeSi)_{1.0}]_n$	AsF_5	100	5×10^{-5}
$[(Me_2Si)_{0.5}(PhMeSi)_{1.0}]_n^{\dagger}$	SbF_5	5	5×10^{-7}
$[(Me_2Si)_{0.5}(PhMeSi)_{1.0}]_n^{\dagger}$	AsF_5	10	2×10^{-1}
$(Me_2Si)_n$	AsF_5	700	7×10^{-3}

† Photocrosslinked polymer

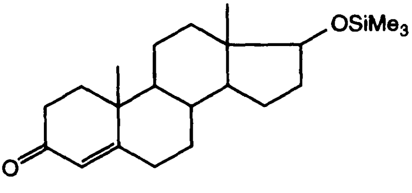
8.6.7 PHARMACEUTICALS

Silicones are chemically stable, physiologically inactive, and hence they are widely used for medical and dental material. For example, medical bottle plugs, catheters, rubber tubes, shunts, blood storage containers, artificial skin, membranes for artificial lungs, contact lenses, dental artificial ivory, etc. [31,62,63,63a]. Moreover, silicones are used as the bases for sustained release drugs, such as growth accelerators, anti-angina pectoris, contraceptives, etc. [64]. Organosilicon compounds are also used as drugs [65–68]. Organosilicon compounds have been developed by the following three methods as drugs [66].

(1) Silylating derivatives of known physiologically active compounds.
(2) The partial substitution by silicon atoms in place of carbon atoms in known physiologically active compounds.
(3) New physiologically active organosilicon compounds.

The object of the first—silylating-derivatives of known physiological active compounds—is to generally increase the solubility to fats and increase the effect of the drugs.

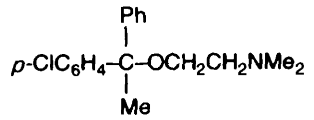
Silylation is the reaction in which the original compounds bond with (i) $OSiMe_3$, (ii) $N(SiMe_3)_2$ or (iii) $SiMe_3$. This treatment considerably changes the physical and chemical properties, and pharmacological solubility to fats increases. The first two silylating methods, O-silylation and N-silylation compounds, reproduce the original compounds by hydrolyzing them easily with body fluids [66]. For example, a medicine of which the trade name is Silandron, shows higher activity than the original hormone preparation [35].



Siladron

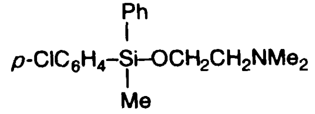
However, the third C-silylating method, producing compounds which directly bond with carbon atoms are stable to hydrolysis by bodily fluids. Then some of them show different activity to the original compounds. For example, phenethylamines ($Ph-CH_2CH_2NH_2$) shows an ability to raise blood pressure. However, the silylating compounds ($R-C_6H_4-CH_2CH_2NH_2$, $R = p$-$SiMe_3$, o-$SiMe_3$) shows the property of *lowering* blood pressure [66].

As the compound substituted partially with silicon atoms in place of carbon atoms in compounds of known physiological activity, for example, in an anticonvulsant drug, the duration of the action of the silylating compound (B) is shorter than the original compound (A). This is considered to be due to the silicon com-



$$p\text{-ClC}_6\text{H}_4\text{-}\underset{\text{Me}}{\overset{\text{Ph}}{\text{C}}}\text{-OCH}_2\text{CH}_2\text{NMe}_2$$

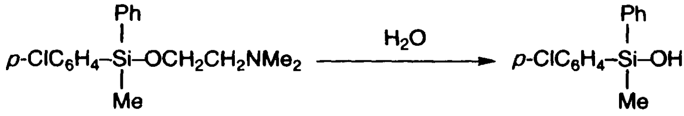
A



$$p\text{-ClC}_6\text{H}_4\text{-}\underset{\text{Me}}{\overset{\text{Ph}}{\text{Si}}}\text{-OCH}_2\text{CH}_2\text{NMe}_2$$

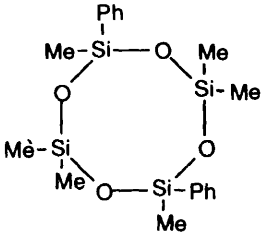
B

pounds being easily hydrolyzed in the living body as shown in eq. (8.56), and the effect of the medicine disappears. The silylating compound B is suitable for drugs which requires the disappearance of the effect of a medicine in a short time [35].



$$p\text{-ClC}_6\text{H}_4\text{-}\underset{\text{Me}}{\overset{\text{Ph}}{\text{Si}}}\text{-OCH}_2\text{CH}_2\text{NMe}_2 \xrightarrow{\text{H}_2\text{O}} p\text{-ClC}_6\text{H}_4\text{-}\underset{\text{Me}}{\overset{\text{Ph}}{\text{Si}}}\text{-OH} \qquad (8.56)$$

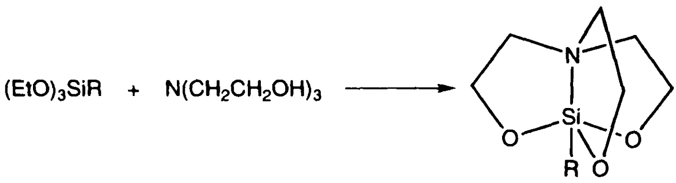
The third research and development area of pharmaceuticals using organosilicon compounds is to find entirely new physiologically active organosilicon compounds which are not similar to any carbon compounds. For example the compound with the trade name Cisobitan (2,6-cis-diphenylhexamethylycyclotetrasiloxane) is used as an anaphrodisiacs and a drug for prostate cancer.



Cisobitane

Silatrane is a five-coordination compound produced as a result of transannular dative bonding, and is prepared by the reaction of trialkoxysilane with tris(hydroxyethyl)amine [12,65,66,68,69]. The chloromethylsilatrane of the silatranes is being tested as a therapeutic agent for epilatory and a vulnerary. Morphorinemethylsilatrane is being tested as a drug for sarcoma [66].

Recently, Fujita and co-workers [70] have been investigating the anti-cancer activity of organosilicon compounds, and $Me_3SiCH_2CH_2SCH_2CH_2NH_2$ (SKD-12A) is found to show the same activity as the anti-cancer drug, 5FU.



(8.57)

R = Ph, CH_2Cl,
$(CH_2)R'$ (R' = morpholino, 1-aziridinyl, NBuAc, CHC_6H_4OH-*p*
n = 1-3

8.6.8 OTHERS

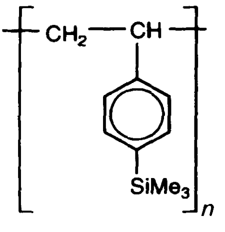
Polymeric organosilicon compounds consist of two kinds of compounds, one of which has a silicon atom in the side chain and the other having a silicon atom in the principal chain as shown in Table 8.6. In these compounds, polysilylmethylene, polysilylphenylene, polysilazane and polymetalosiloxane (e.g., Si—O—Ti—O) are used as preceramic polymers of SiC, Si_3N_4 and Si—C—Ti—O [42].

On the other hand, the poly(1-trimethylsilyl-1-propylene) of a pendant polymer has high gas permeability, and is expected to be used as an oxygen enrichment membrane [61]. In lithography, which is pattern transcription technology, a photoresist of one of the photosensitive polymers is used for preparation of semiconductor elements. As to the photoresist made of organosilicon compounds, its etching speed is high, and the image pattern of silicon oxide produced by an oxygen plasma etching, is firm. Many organosilicon compounds have been developed as photoresist polymers. The polymers having a silicon atom in their side chains are shown in Table 8.7. The polymers having a silicon atom in their principal chains are shown in Table 8.8. Generally, the latter polymers contain more silicon atoms. Then the amount of silicon oxide which is produced by oxygen plasma etching is larger and hence the stability of the resist image is better [61].

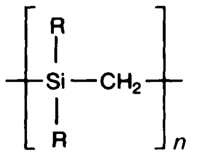
Liquid crystal polymers consist of two kinds. One is a principal chain liquid crystal polymer such as poly(*p*-phenyleneterephthalamide) and the other is a side chain liquid crystal polymer having a liquid crystal component (mesogen) as the side chain. The liquid crystal polysiloxanes belong to the latter type of polymer.

The representative principal chain liquid crystal polymers are aromatic polyamides and aromatic polyesters which have been developed as high strength and with a high modulus of elasticity. However, side chain liquid crystal polymers have been developed as optoelectronic materials such as a low molecular weight liquid crystal element for watches, electric calculators, televisions, etc. As the liquid crystal phase of the polymer liquid crystal chain can be easily fixed than for low molecular weight liquid crystals, they are expected to be higher functional materials [61]. Side chain type liquid crystal polymers have the bent chain which gives the degree of freedom of the liquid crystal orientation between the principal chain and the mesogen. If acrylic polymer is used as the principal chain, the temperature range in which it can be used as a liquid polymer is elevated due to the influence of

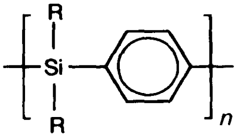
Table 8.6 Organosilicon polymers [61]



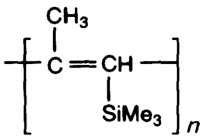
poly-*p*-trimethylsilylstyrene



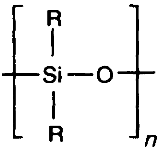
polysilylmethylenes



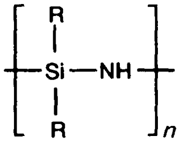
polysilylphenylene



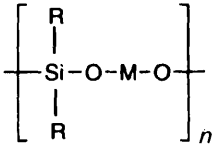
poly(1-trimethylsilyl-1-propyn)



polysiloxanes



polysilazanes

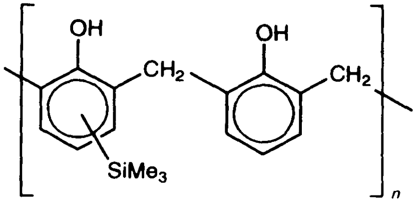


polymetalosiloxane

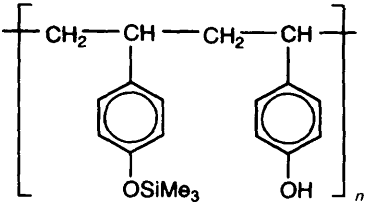
the integrity of the main chain. However, in polysiloxanes, as its internal rotation potential is small, the degree of freedom of the mesogen increases and the orientation become easy. So they show liquid crystal properties even at room temperature, and the range of temperature for its use as a liquid crystal become wide. They have been investigated for their use for various kinds of liquid crystal display elements [61]. For example, as shown in eq. (8.58), liquid crystal polysiloxane is prepared by hydrosilylation of polyhydrosiloxane with olefins. The mesogen which shows liquid crystal property is $-O-C_6H_4-C_6H_4-CN$ (*p*,*p*), and the bent chain is $-CH_2-CH_2-$ [61].

Chlorosilanes and aminosilanes are used for the preparation of drugs as silylating agents which can substitute an active hydrogen such as an amino, carbonyl and hydroxide group with a silyl group (R_3Si-). Recently, organosilicon compounds for the application of organosynthetic reactions have been investigated not only on these silylating agents but also on highly selective reactions applying the

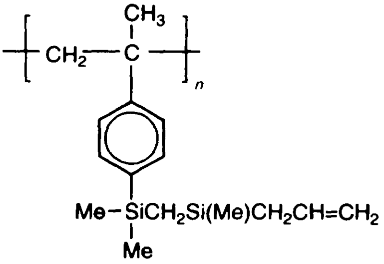
Table 8.7 Photoresist polymers with a silyl side chain [61]



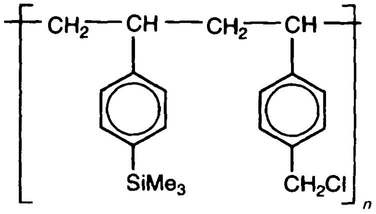
Novolak type



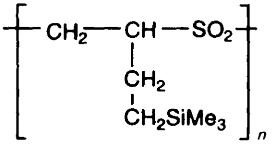
Polyvinylphenol type



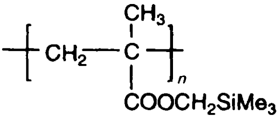
poly-α-methlstyrene



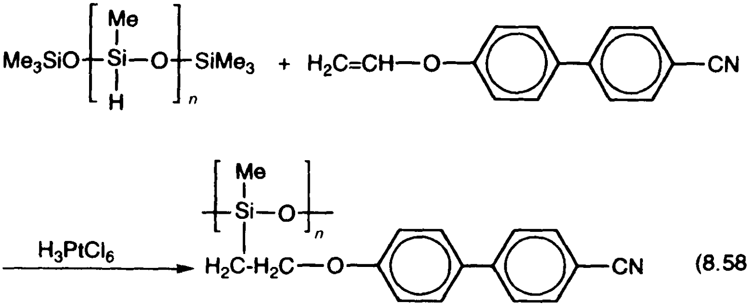
Polystyrene type



Polyolefinsulfonyl type

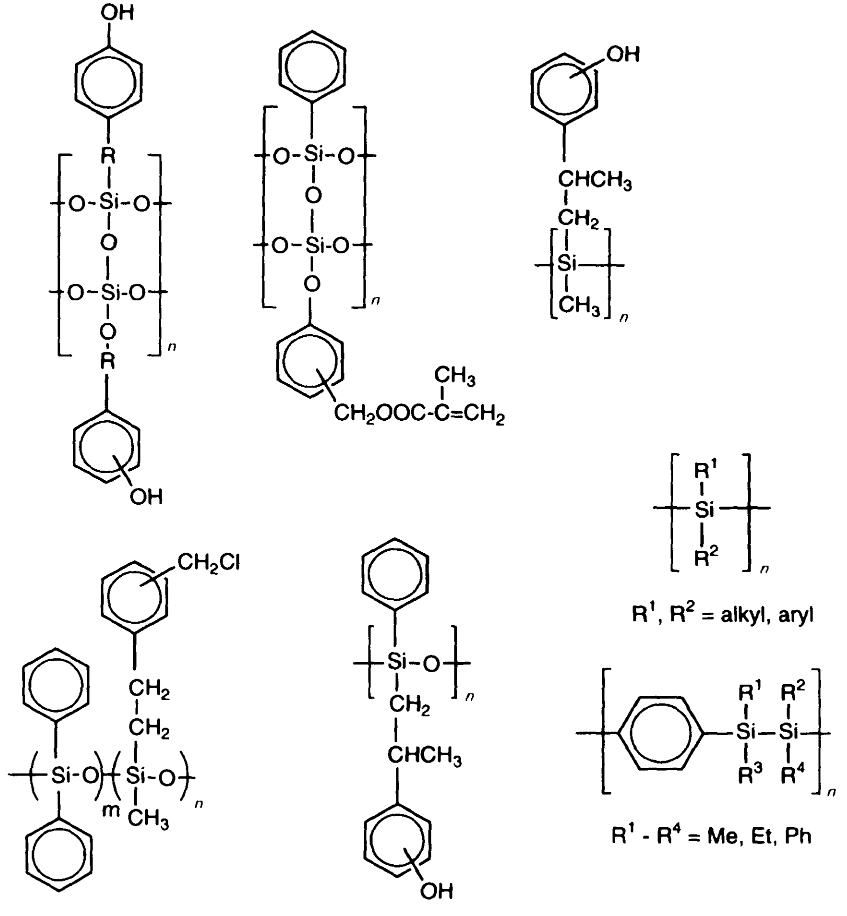


Polymetacrylate type



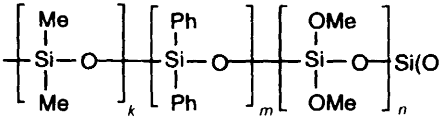
(8.58)

Table 8.8 Photoresist polysiloxane and polysilanes [61].

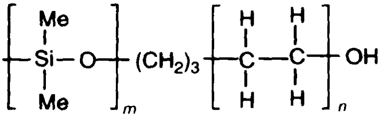


characteristics of silicon, and many books and reviews on these have been published [35,71–84].

Recently, the more rapidly advancing fields of application of organosilicon compounds are antifouling paints [85–88], cosmetics [89,90] and CVD [91], etc. Organosilicon compounds have a small surface tension and, as described above, this characteristic gives rise to the anti-fouling effect. Thus, silicone resins are used as antifouling paints. Anti-thrombotic materials form two phases of a lamella type phase separation structure. On the other hand, if the silicone resins can form a phase separation structure of hydrophilic and hydrophobic properties, they will show anti-fouling properties. In particular, one containing 15–20 % of hydrophilic silicone resins shows the most effective properties [85].



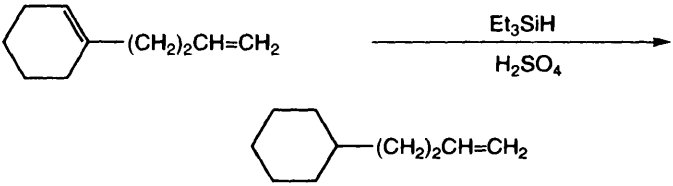
Hydrophobic silicone resins



Hydrophilic silicone resins

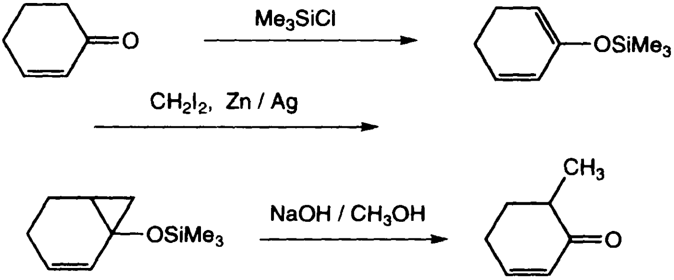
The representative synthetic reactions with organosilicon compounds are the following four reactions.

(1) Reduction. The silicone hydrides of Et_3SiH, Ph_2SiH_2, $Et_3SiO{-}(SiH_2O{-})_{10}SiEt_3$ and $Me_3SiO{-}(SiMe(H)O)_{35}SiMe_3$, etc. are suitable for reductions such as the synthetic reactions of aldehydes from nitriles, and selective hydrogenations (e.g., eq. (8.59) [92]).



(8.59)

(2) Silylation. Not only chlorosilanes and silazanes as described above, but also Me_3SiCN are used as silylating agents. On the other hand, the active groups which react with silylating agents are not only the amino, carboxylic and hydroxy groups described above, but also ketocarbonyl, mercapto, and carboamino groups. For example, as shown in eq. (8.60), if the ketocarbonyl group is protected with the silylating agent, a cyclopropane ring is formed by reaction with a Simmon–Smith reagent, and the methyl derivatives of the original ketocarbonyl is obtained by its hydrolysis [93].



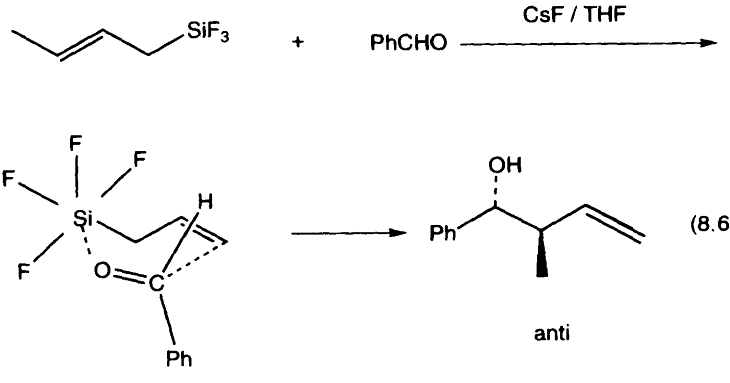
(8.60)

(3) Alkylation. There are saturated and unsaturated alkylating agents used. The saturated alkylation agents are tetraalkylsilanes, etc., for example the reaction with acid chlorides gives the ketones as shown in eq. (8.61) [94].

$$R_4Si + R'COCl \longrightarrow R'COR + R_3SiCl \qquad (8.61)$$

$$R = Et, Bu, \; R' = Et, Ph$$

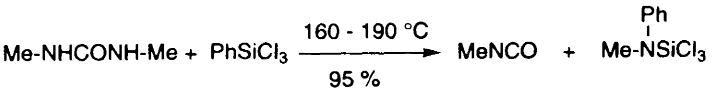
The unsaturated alkylating agents are used for many organosynthetic reactions with organosilicon compounds. The unsaturated alkylating agents are allyl, vinyl, alkenyl, allene, etc. Since the trialkylsilanes having these groups are very reactive, they can easily give an unsaturated group to organic compounds. Organosilicon compounds are coordinated by the oxygen or nitrogen atom, and they tend to form five- or six-coordination bonds. Therefore, the reaction to form the coordination with these atoms is sterically regulated, and stereospecific reactions tend to proceed. For example, (*E*)crotyltrifluorosilane reacts with benzaldehyde, and the silicon atom forms six-coordination with a six-membered ring by coordination of oxygen atom of benzaldehyde. As the direction of the bond is fixed, the ratio of anti is 99 %, shown in eq. (8.62) [95,96]. Further, with compounds which tend to form a bidentate coordination such as catechol or to form a multi-dentate coordination, if the silicon compounds react with the compounds, as the direction of the reaction is fixed, the reaction proceeds stereospecifically [97].



(8.62)

(4) Others. Organosilicon compounds are able to react with compounds having a functional group such as amino, halogen and phosphine. For example, phosphinotrimethylsilane reacts with benzoylchloride to give diphenylphosphine in high yield as shown in eq. (8.63) [98]. The other reactions are an anti-Markovnikoff type halogenation reaction with olefins, and an isocyanate synthetic reaction with urea or carbamates (eq. (8.64)), etc., [99].

$$Me_3SiPPh_2 + PhCOCl \xrightarrow{96\ \%} PhCOPPh_2 \quad (8.63)$$



$$Me\text{-}NHCONH\text{-}Me + PhSiCl_3 \xrightarrow[95\ \%]{160 - 190\ °C} MeNCO + Me\text{-}\overset{Ph}{N}SiCl_3 \quad (8.64)$$

REFERENCES

[1] *New Silicone and its Applications*, Toshiba Silicone Co.Ltd., 1994.
[1a] H. Terao, *Kagaku Keizai*, March (1995) 184.
[2] H. Sano, *Kagaku Keizai*, May (1990) 63.
[3] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
[4] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol. A23, p. 721, 1990.
[5] *12695 no Kagaku Shohin*, Kagaku Kogyo Nipposha, Tokyo, 1995.
[6] *Kagaku Daijiten*, Tokyo Kagaku Dojin, p. 695, 1989.
[7] *Sekai Daihyakka Jiten*, Heibonsha, Tokyo, p. 523, 1988.
[8] *Rikagaku Jiten*, 4th ed. Iwanami Shoten, Tokyo, p. 376, 1987.
[9] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol. A24, p. 21, 1990.
[10] M. Arai, *Yuki Gosei Kagaku Kyokaishi*, **40** (1982) 567.
[11] E.G. Rochow, *U.S. Patent*, 2380995 (1945).
[12] D.A. Armitage, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 9, p. 1, 1982.
[13] T.G. Welin and R. West, *J. Am. Chem. Soc.*, **84** (1962) 1860.
[14] M. Kumada, M. Ishikawa, K. Yamamoto and K. Tamao, *Yuki Keiso Kagoubutsu no Kagaku*, Kagaku Dojin, Kyoto, 1972.
[15] T. Hayashi, K. Katabe, T. Yamamoto, K. Tamao and M. Kumada, *Tetrahedron Lett.*, (1983)5661.
[16] T.K. Sarkar, *Synthesis*, (1990) 969.
[17] K. Yamamoto, *Shokubai*, **34** (1992) 166.
[18] M.P. Doyle and M.S. Shanklin, *Organometallics*, **12** (1993) 11.
[19] A. Sekiguchi, I, Maruki and H. Sakurai, *J. Am. Chem. Soc.*, **115** (1993) 11460.
[20] H. Sakurai, *Gendai Kagaku*, July(1994)16.
[21] A. Sekiguchi and H. Sakurai, *Adv. Organomet. Chem.*, **37** (1995) 1.
[22] H. Suzuki, N. Tokitoh and R. Okazaki, *J. Am. Chem. Soc.*, **116** (1994) 11572.
[23] A.G. Brook. *J. Am. Chem. Soc.*, **80** (1958) 1886.
[24] R. West, R. Lowe, H.F. Stewart and A. Wright, *J. Am. Chem. Soc.*, **93** (1971) 282.
[25] M. Ishikawa and M. Kumada, *J. Chem. Soc. Chem. Commun.*, (1969) 567.
[26] C.G. Pitt and M.S. Fowler, *J. Am. Chem. Soc.*, **90** (1968) 1928.
[27] F.C. Whitmore, L.H. Sommer and J. Gold, *J. Am. Chem. Soc.*, **69** (1947) 1976.
[28] M. Kumada, J. Nakajima, M. Ishikawa and Y. Yamamoto, *J. Org. Chem.*, **23** (1958) 292.
[29] H. Sakurai ed., *Yuki Keiso Polymer no Gosei to Ooyo*, CMC, Tokyo, 1989.
[30] M. Kajiwara and K. Murakami ed., *Muki Kobunshi*, Sangyo Tosho, 1992.
[30a] K. Sakamoto, M. Yoshida and H. Sakurai, *Kobunshi*, **41** (1992) 78.
[30b] M. Ishikawa, T. Hatano Y. Hasegawa, T. Horio, A. Kunai, A. Miyai, T. Ishida, T. Tsukihara, T. Yamanaka, T. Koike and J. Shioya, *Organometallics*, **11** (1992) 1604.

[31] H. Maruyama, M. Dogawa and H. Sano ed., *Silicone and its Applications* (*Silicone to sono Ooyo*), Toshiba Silicone Co. Ltd., 1988.

[32] K. Tamura, *Silicone* (*Keiso Jushi*), Nikkan Kogyo Shinbunsha, Tokyo, 1961.

[33] I. Nakajima and K. Ariga, ed., *Silicone* (*Keiso Jushi*), Nikkan Kogyo Shinbunsha, Tokyo, 1970.

[34] M. Kumada and T. Wada ed., *New Technology on Silicone* (*Saishin Silicone Gijutsu*), CMC, Tokyo, 1986.

[35] S. Pawlenko, *Organosilicon Chemistry*, Walter de Gruyter, Berlin, 1986.

[36] E.G. Rochow, *J. Am. Chem. Soc.*, **67** (1945) 963, 1772.

[37] E.G. Rochow, *An Introduction to the Chemistry of the Silicons*, John Wiley, New York, 1951.

[38] E.G. Rochow and W.F Gilliam, *J. Am. Chem. Soc.*, **67** (1945) 1772.

[39] C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960.

[40] M.P. Clarke, *J. Organomet. Chem.*, **376** (1989) 165.

[41] D.R.M. Walton, *J. Chem. Soc. C* (1966) 1706.

[42] K. Okamura, *Kobunshi*, **37** (1988) 464.

[43] H. Ichikawa, *Kobunshi*, **42** (1993) 584.

[44] *Kagaku Kogyo Jiho*, Aug. 15, 1993.

[45] M. Kumada and K. Tamao, *Adv. Organomet. Chem.*, **6** (1968) 19.

[46] M. Kumada, *Kobunshi*, **37** (1988) 447.

[47] M. Ishikawa, *Kobunshi*, **37** (1988) 456.

[48] R. West, L.D. David, P.I. Djurovich, K.L. Stearley, K.S.V. Shinivasan and H. Yu, *J. Am. Chem. Soc.*, **103** (1981) 7352.

[49] R. West, *J. Organomet. Chem.*, **300** (1986) 327.

[50] R. West and T.J. Barton, *J. Chem. Educ.*, **57** (1980) 165.

[51] R. West and T.J. Barton, *J. Chem. Educ.*, **57** (1980) 334.

[52] M. Ishikawa, *Kagaku to Kogyo*, **27** (1974) 3.

[53] M. Ishikawa, *Kagaku*, **45** (1990) 247.

[54] M. Ishikawa, *Shokubai*, **32** (1990) 203.

[55] T. Shinozaki, *Nikkei New Materials*, Aug. 15(1988)40.

[56] H. Sakurai, *Kagaku to Kogyo*, **42** (1989) 744.

[57] H. Matsumoto, *Kagaku to Kogyo*, **43** (1990) 625.

[58] R.D. Miller and J. Michl, *Chem. Rev.*, **89** (1989) 1359.

[59] R.G. Kepler, *Synthetic Metal*, **28** (1989) C573.

[60] A. Nishimura, *Plastics*, **32** (1982) 52.

[61] H. Sakurai ed., *Synthesis and Application of Organosilicon Polymer*, (*Yuki Keiso Polymer no Gosei to Ooyo*), CMC, Tokyo, 1989.

[62] A. Igarashi, *Kino Zairyo*, **12**(2)(1992)39.

[63] A. Kishida and M. Akashi, *Kino Zairyo*, **13**(4)(1993)5.

[63a] I. Ando, *Kagaku Kogyo*, **45** (1994) 233.

[64] F.S. Rankin, *Manufacturing Chemist*, August (1987)49.

[65] M. Kumada, *Kagaku*, **28** (1973) 213.

[66] T. Inoi and Y. Nagai, *Yuki Gosei Kagaku*, **40** (1982) 582.

[67] H. Sakurai ed. *Organosilicon and Bioorganosilicon Chemistry*, R. Tacke, p.251, John Wiley, New York, 1984.

[68] E. Lukevics, A. Lapsina, G. Zeicans, A. Dauvarte and A. Zidermane, *Latv. PSR Zinast. Akad. Vestis, Kim. Ser.* (1978)338; *Chem. Abstr.*, **89** (1978) 129581g.

[69] C.L. Frye, G.E. Vogel and J.A. Hall, *J. Am. Chem. Soc.*, **83** (1961) 996.

[70] H. Fujita, K. Fukushima, T. Sakurai, M. Fukuma, Y. Seto, T. Fujita, K. Itoh, N. Shinohara, Y. Yamamoto and T. Ishihara. *Nihon Kagakukaishi*, (1990)566.

[71] E.W Colvin, *Silicon in Organic Synthesis*, Butterworths, London, 1981.

[72] W.P. Weber, *Silicon Reagents for Organic Synthesis*, Springer-Verlag, Berlin, 1983.

[73] G. Wilkinson, F.G.A. Stone and E.W. Abel ed., *Comprehensive Organometallic Chemistry*, P.D. Magnus, T. Sarker and S. Djuric, vol. 7, p.515, Pergamon Press, Oxford, 1982.
[74] M. Kumada, M. Ishikawa, K. Yamamoto and K. Tamao, *The Chemistry of Organosilicon Compounds* (*Yukikeiso Kagoubutsu no kagaku*), Kagakudojin, Tokyo, 1972.
[75] H. Sakurai, *Kagakuzokan*, **105** (1985) 33.
[76] M. Kira, *Kagaku to Kogyo*, **45** (1990) 614.
[77] M. Ochiai and E. Fujita, *Yuki Gosei Kagaku Kyokaishi*, **40** (1982) 508.
[78] H. Sakurai, *Pure Appl. Chem.*, **54** (1982) 1.
[79] H. Sakurai, *Pure Appl. Chem.*, **57** (1985) 1759.
[80] A. Hosomi and H. Sakurai, *Yuki Gosei Kagaku Kyokaishi*, **43** (1985) 406.
[81] N. Imai, Y. Terao and K. Achiwa, *Yuki Gosei Kagaku Kyokaishi*, **43** (1985) 862.
[82] Y. Kita, O. Tamura and Y. Tamura, *Yuki Gosei Kagaku Kyokaishi*, **44** (1986) 1118.
[83] K. Tamao, *Yuki Gosei Kagaku Kyokaishi*, **46** (1988) 861.
[84] E. Keinan, *Pure Appl. Chem.*, **61** (1989) 1737.
[85] H. Nakaymaa, *Kagaku Kogyo*, **46** (1995) 112.
[86] *Japan Kokai Patent*, 4-142373.
[87] *Japan Kokai Patent*, 1-190612.
[88] *Japan Kokai Patent*, 63-2995.
[89] H. Aoki, *Kobunshi*, **42** (1993) 670.
[90] H. Aoki, *Kino Zairyo*, **11**(12) (1991) 5.
[91] K. Maeda, *Kagaku Kogyo*, **43** (1993) 372.
[92] D.N. Kursanov, Z.N. Parnes and G.I. Bolestova, *Dokl. Akad. Nauk SSSR*, **181** (1968) 1132; *Chem. Abstr.*, **69** (1968) 105969a.
[93] C. Girard and J.M. Conia, *Tetrahedron Lett.*, (1974) 3327.
[94] G.A. Olah, T.-L. Ho, G.K. Surya Prakash and B.G. Balaram Gupta, *Synthesis*, (1977)677.
[95] M. Kira, M. Kobayashi and H. Sakurai, *Tetrahedron Lett.*, (1987) 4081.
[96] M. Kira, T. Hino and H. Sakurai, *Tetrahedron Lett.*, (1989) 1099.
[97] H. Sakurai, *59th Annual Spring Meeting of Chemical Society of Japan*, vol.3, p. 2261 (1990).
[98] H. Kunzek, M. Braun, E. Nesener and K. Rühlmann, *J. Organomet. Chem.*, **49** (1973) 149.
[99] V.F. Mironov, *J. Organomet. Chem.* **271** (1984) 207.

9 Organogermanium Compounds

9.1 INTRODUCTION

Germanium is an element in group 14 of the periodic table and many compounds of germanium similar to silicon and tin compounds have been synthesized [1]. However, germanium is a highly expensive metal compared with silicon or tin, and the amount used is small. Now, the research and development in the field of pharmaceuticals have been energetically conducted. Its other uses are as catalysts for isomerization of sugars, etc.

9.2 GERMANIUM

There are no ores containing germanium as a main component. Argyrodite ($4Ag_2S{\cdot}GeS_2$, Ge content 1.8–6.9 %) and germanite ($Cu_3(Ge,Fe)S_4$, Ge content, 5–10 %) are ores for silver or copper. In the production of silver or copper, Ge_2O_3 is contained in these by-products. The Ge_2O_3 concentrate (20–30 %) is prepared by the distillation of the by-product with CO gas. The Ge_2O_3 is chlorinated and pure $GeCl_4$ is prepared by distillation. Pure Ge_2O_3 is prepared by the hydrolysis product of $GeCl_4$ with pure water. Pure Ge_2O_3 is then obtained by drying the hydrolysis product. Ge polycrystal is prepared by reduction of Ge_2O_3 with an ammonia decomposition gas ($H_2 + N_2$) or hydrogen. High purity single crystal germanium is obtained by the repeated passage of crude germanium through the zone-refining crucible [2]. The physical properties of germanium are shown in Table 9.1 [3].

The world demand for germanium is about 80 tons per year. The price of germanium oxide was about 700 $/kg. However, the demand for optical fibers and PET bottles increased, and in June 1995, the price was 800–950 $/kg [2,2c]. The uses of germanium are as shown in Table 9.2 [2,2a]. Germanium oxide is mainly used here. The largest use before 1990 was as polymerization catalysts for PET bottles. In PET, if it is produced by polymerization with germanium oxide as the catalyst, its transparency is increased and it can be used as containers for food since it is nontoxic.

The second was for medical uses such as crude drugs. Recently in the fad for health foods, many people ingested many kinds of foods containing germanium. Several people were poisoned to death since they had ingested these health foods for a long time, and had taken many times a maximum permissible dose. Thus, some companies were prosecuted for a violation of the Drugs, Cosmetics and

Table 9.1 Properties of germanium [3]

Property	Value
melting point, °C	937.4
boiling point, °C	2830
crystal structure	diamond cubic
density at 25 °C, g/cm^3	5.323
lattice constant at 25 °C, nm	0.565754
Mohs hardness	6.3
Poisson's ratio at 125–375 K	0.278
thermal conductivity at 300 K, W/(m.k)	59.9
intrinsic resistivity at 25 °C, ohm.cm	53

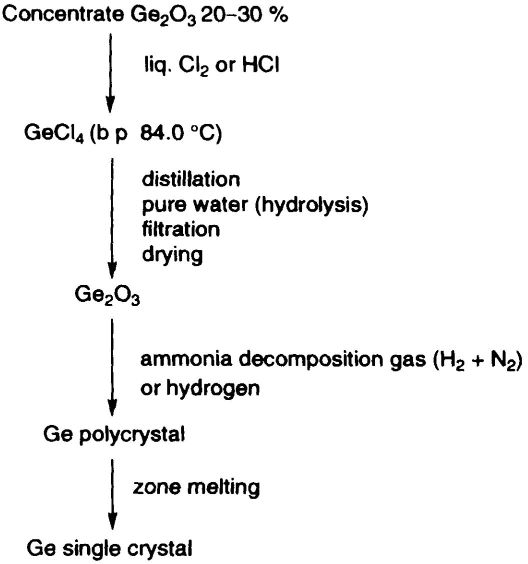


Figure 9.1 Production of germanium [2].

Medical Instruments Act by the authority. Germanium oxide is used as a drug for anemia since it has a hematogenic action. However, this use decreased in Japan after this exaggerated propaganda case of the medical benefits of germanium oxide, as shown in Table 9.2 [4–10].

The third use was for optical fibers. But, since 1990, the information networks have increased in the world and the demand for optical fibers has increased rapidly. The consumption used in optical fibers becomes more than that of the catalyst for PET bottles and it becomes the largest use. The core of an optical fiber is the

Table 9.2 Consumption estimates for Ge [2,2a] (tons, calculated in terms of Ge)

Uses	1987	1989	1992	1994
catalysts for polycondensation of PET for bottles	11	13	16	19
pharmaceuticals	4	3	3	3
optical fibers	3	3	20	25
infrared lenses, windows	1	1	20	17
germane gas, semiconductors	1	0.5	5	5
catalysts for petrochemicals, and others	0.5	0.5	12	11
totals	20.5	21	76	80

passage of light. The refractive index of the core is required to be higher than that of the surrounding material to protect the light from dispersion. Germanium tetrachloride is added to the core part and it is oxidized. If the germanium compound is added by 10%, the refractive index increases by about 1%. Germanium compounds are added by 3% for the single mode of long distance large capacity circuit and by 10% for a multi-mode junction circuit used in an urban area [11].

Other uses are for infrared lenses since a glass with added germanium oxide has a high transmission of infrared radiation, and also for cracking catalysts in oil refining and as germanium gas for the preparation of solar cells, transistor, diode, etc.

9.3 PREPARATIONS FOR ORGANOGERMANIUM COMPOUNDS

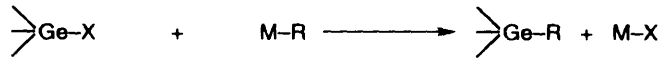
There are three methods for preparing organogermanium compounds using germanium metal or inorganic germanium compounds as raw materials. These methods are direct reactions shown in eq. (9.1), reactions of germanium halide with organometallic compounds shown in eq. (9.2) and hydrogermylation reactions shown in eq. (9.3) [12].

The direct reactions of organogermanium compounds also use copper as a catalyst similar to those of organosilicon compounds described in the previous chapter. The main products are R_2GeX_2 when the alkyl groups are lower alkyl groups such as methyl or ethyl [13]. For example, EtCl reacts with germanium metal at 317 °C for 48 h to give Et_2GeCl_2 and $EtGeCl_3$. Yields of these reactions are 47% and 18%, respectively [14]. When the alkyl is propyl, the main product is $PrGeCl_3$ [15].

$$\mathrm{RX} \quad + \quad \mathrm{Ge} \longrightarrow \mathrm{R}_n\mathrm{GeX}_{4-n} \qquad (9.1)$$

R = alkyl, aryl
X = halogen
$n = 0, 1–4$

The second method is that germanium halides react with organometallic compounds of alkali metals, Mg, Zn, Hg or Al as shown in eq. (9.2). In these reactions, the reactions with Grignard reagents are suitable for the syntheses of tetraalkyl germanium compounds and actually these reactions are used frequently. For example, $GeCl_4$ reacts with the excess of MeMgI to give Me_4Ge in 93 % yields [16].



(9.2)

R = Li, Na, K, Mg, Zn, Hg, Al
X = halogen

The third method is the hydrogermylation reaction shown in eq. (9.4). The germanium metal reacts with hydrogen chloride gas to give halogermanium hydride, and organogermanium compounds are obtained by the addition of the halogermanium hydride to an unsaturated compound [17]. The reaction process shown in eqs. (9.3) and (9.4) is a very convenient process and the same process is

$$Ge + 3HCl \xrightarrow[450-500\ °C]{Cu} HGeCl_3 + H_2 \qquad (9.3)$$

$$HGeCl_3 + CH_2{=}CH\text{-}Y \longrightarrow Cl_3GeCH_2\text{-}CH_2\text{-}Y \qquad (9.4)$$

Y = alkyl, aryl, COOR, COR, CN, etc.
R = alkyl, aryl

used for the syntheses of organosilicon compounds [18] or organotin compounds [19]. Before this process was found, in the case of organotin trihalides, the trihalides were prepared via hydrometalation, and by substitution of an alkyl group with halogen as shown in Scheme 9.1.

The other methods are that organogermanium compounds are prepared by heating germanium tetrahalides with alkyl halides in the presence of a copper catalyst [12].

$$GeX_4 + RX \xrightarrow[heat]{Cu} RGeX_3 \qquad (9.5)$$

Further, organogermanium compounds react with various kinds of compounds to give many germanium derivatives containing the following bonds: Ge–H, Ge–O, Ge–S, Ge–Se, Ge–Te, Ge–N, Ge–P, Ge–As, Ge–Sb, Ge–Bi and Ge–M (M = Li, Na, K, Rb, Cs, Sr, Ba, Al, Hg, Tl, Ge, Sn, Cr, Mo, W, Cd, etc.) [12]. The germanium hydrides (Ge–H) react with compounds having a multiple bond such as alkene, alkyne, carbonyl, imine and nitro groups. These reactions are the hydrogermylation reactions and easily proceed as shown in eq. (9.6) [12].

$$\mathrm{M} + 2\mathrm{X_2} \longrightarrow \mathrm{MX_4}$$

$$3\mathrm{R_4M} + \mathrm{MX_4} \longrightarrow 4\mathrm{R_3MX}$$

$$\mathrm{R_3MX} + \mathrm{LiAlH_4} \longrightarrow \mathrm{R_3MH}$$

$$\mathrm{R_3MH} + \mathrm{CH_2{=}CH{-}Y} \longrightarrow \mathrm{R_3MCH_2CH_2{-}Y}$$

$$\mathrm{R_3MCH_2CH_2{-}Y} + 3\mathrm{X_2} \longrightarrow \mathrm{X_3MCH_2CH_2{-}Y}$$

M = Sn, Y = functional group

Scheme 9.1

$$\mathrm{R_3GeH} + \mathrm{CH_2{=}CH(CH_2)}_n\mathrm{Y} \longrightarrow \mathrm{R_3Ge(CH_2)}_{n+2}\mathrm{Y} \qquad (9.6)$$

R = alkyl, aryl
Y = halogen, OH, COOR, COR, CN, etc.
$n = 0, 1, 2,$ etc.

For example, the hydrogermylation of pentene-1 gives a pentyl derivative in high yield [20].

$$\mathrm{Ph_3GeH} + \mathrm{CH_2{=}CH(CH_2)_2Me} \xrightarrow{\mathrm{UV}} \underset{95\,\%}{\mathrm{Ph_3GeC_5H_{11}}} \qquad (9.7)$$

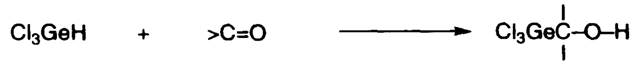
9.4 PROPERTIES OF ORGANOGERMANIUM COMPOUNDS

Most of the organogermanium compounds are tetravalent. Very few higher coordination compounds than five have been reported, compared with organosilicon or organotin compounds. The electronegativity of germanium is 2.02 and it is close to carbon (2.50) and hydrogen (2.20), and it is higher compared to silicon (1.74), tin (1.72) and lead (1.55). Therefore, the bond between germanium and hydrogen (Ge—H) has very little polarity compared with those of Si—H, Sn—H and Pb—H. Hence, if germanium bonds to alkyl groups of strong electron donation or halogens of strong electron-withdrawing properties, the polarities of germanium atoms in the Ge—H bonds are different as follows [12]:

$$\overset{\delta+}{\mathrm{R_3Ge}}\text{——}\overset{\delta-}{\mathrm{H}} \qquad\qquad \overset{\delta-}{\mathrm{X_3Ge}}\text{——}\overset{\delta+}{\mathrm{H}}$$

Therefore, as shown in eqs. (9.8) and (9.9), in these hydrogermylation reactions, the direction of bonding to the carbonyl group is also different [12].

$$\mathrm{Et_3GeH} \quad + \quad \mathrm{{>}C{=}O} \longrightarrow \mathrm{Et_3Ge{-}O{-}\overset{|}{\underset{|}{C}}{-}H} \tag{9.8}$$



$$\mathrm{Cl_3GeH} \quad + \quad \mathrm{{>}C{=}O} \longrightarrow \mathrm{Cl_3Ge\overset{|}{\underset{|}{C}}{-}O{-}H} \tag{9.9}$$

The bond energy of Ge$-$CH$_3$ is 59 kcal/mole (247 kJ/mole) and is intermediate between Si$-$C (70 kcal/mole (293 kJ/mole)) and Sn$-$CH$_3$ (50–52 kcal/mole (209–218 kJ/mole)). Therefore, the stability of Ge$-$C is also considered to be intermediate. However, if the functional group bonds at the α, β or γ position, the stability is abnormally lowered by an intermolecular rearrangement or a decomposition [12].

9.5 APPLICATIONS OF ORGANOGERMANIUM COMPOUNDS

9.5.1 PHARMACEUTICALS

Crude drugs and health foods such as polypore, ginseng and garlic, as shown in Table 9.3 [21–26], contain much germanium. However, the structure of germanium compounds contained in these plants has not been determined yet. However, it has become apparent that these compounds have Ge$-$O bonds. Thus, these compounds are considered to be complexes of saccharoids. Therefore, as the complexes of germanium, the complexes of monosaccharides, saccharoid alcohol [27], oxycarboxylic acid [28], compounds of germanium acid alkali salts and organic acids such as citric acid, ascorbic acid and malic acid [29], complexes of organochelate agents [30] such as ethylenediamine tetraacetate (EDTA) and nitrotriacetate (NTA), complexes of germanium tetrachloride with salicylic acid [31], mercapto complexes [25,26,32,33], porphyrin complexes [34], etc., have been synthesized.

In the case of cultivating the Japanese radish with germanium oxide, the germanium content is found to be 417.4 ppm. If it is cultivated with 2-carboxyethylgermanium sesquoxide (Bis(2-hydroxycarbonylethylgermanium)trioxide), the germanium content increases to 1120.0 ppm [24]. If chlorella and spirulina are cultivated with the complexes of germanium acid alcohol and organochelating agents, the germanium content is1500 ppm and 2500 ppm in their dehydrated state, respectively [30]. As shown in Table 9.3, the plants which are used as crude drugs, contain many germanium compounds. Therefore, it is considered that some germanium compounds increase immunological functions and inhibit diseases such as cancers. Asai and Kakimoto in Asai Germanium Research Institute have screened many germanium compounds, and they found 2-carboxyethylgermanium sesquioxide in 1967, presented at the Chemical Society of Japan in 1968, and patented in

Table 9.3 Germanium concentration in selected plants [21–26]

plants	Ge concentration (ppm)
polypore	800–2000
ginseng (Korea, 20 years or more)	2000–4000
ginseng	250–320
litchi	800–2000
garlic	745–756
Acanthopanax senticosus	310–400
Chebulae fructus	260
Bandai mushroom	255
Sophorae subprostratae	250
water caltrop	230–257
Chinese maltrimony vine	120–124
comfrey	76–152
Lithospermi radix	58
adlay	50

Japan in 1971 [22,35]. 2-Carboxyethylgermanium sesquioxide has the planar structure of a twelve-membered ring in which Ge bonds to three oxygens as shown in Figure 9.2 [36]. The carboxylate chains, which bond to germanium, are alternately on the top and bottom of the twelve-ring plane. The carboxylate chains form hydrogen bonds with carboxylate chains [36] top and bottom. The crystal of 2-carboxyethylgermanium sesquioxide forms plates, usually insoluble in organic solvents, soluble in water by heating and which does not fuse or decompose under 320 °C [36]. It is considered that these properties are caused by a three-dimensional high polymeric state as shown in Figures 9.2 and 9.3.

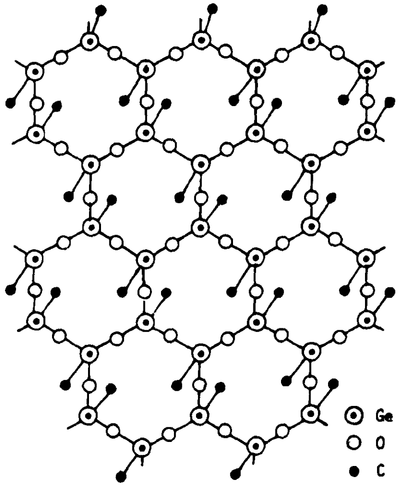


Figure 9.2 A stereoview showing the layer network of $(GeCH_2CH_2COOH)_2O_3$. The carboxylate and carbon chain have been omitted for clarity [36].

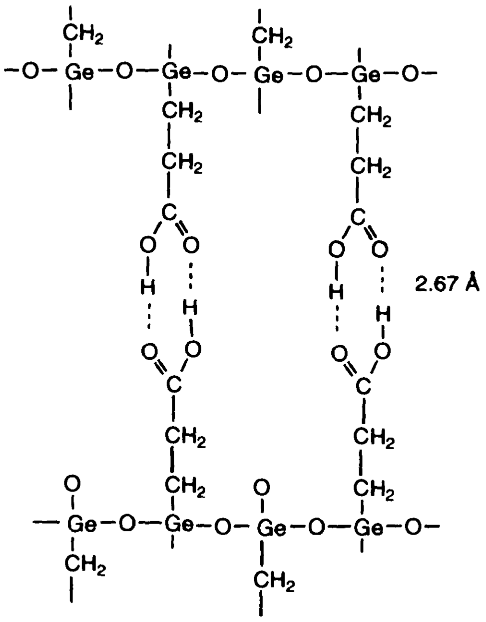


Figure 9.3 The infinite sheet network with 12-member rings bound together vertically by hydrogen bonds between the carboxyl gorups attached to each sheet [36].

2-Carboxyethylgermanium sesquioxide is prepared as shown in Scheme 9.2. Germanium reacts with hydrogen chloride gas at high temperatures to give trichlorogermanium hydride described above (eq. 9.3) and the hydrogermylation reaction of acrylic acid with trichlorogermanium hydride proceeds, and 2-carboxyethylgermanium sesquioxide is obtained by hydrolysis as shown in Scheme 9.2 [36]. Besides, 2-carboxyethylgermanium sesquioxide is also prepared from acrylnitrile, acrylamides or methylvinylketone in place of acrylic acid as shown in Scheme 9.2. Furthermore, it is also prepared with hypophosphorous acid [21,22, 35–47].

In 1977, 2.2 million Ehrlich ascitic cancer cells were transplanted intraperitoneally to mice. Subsequently, the dose group of 2-carboxyethylgermanium sesquioxide showed a growth inhibition effect by 30% compared with the control group [22]. Furthermore, in experiments with mice exposed to carcinogenic 3-methylchloroanthracene performed in 1978, 2-carboxyethylgermanium sesquioxide was found to increase greatly the prolongation of life [48]. Their virtue as anticancer drugs was also found with lactose as a carrier of 2-carboxyethylgermanium sesquioxide [49] and with amino acid salts such as the lysine salt of 2-carboxyethylgermanium sesquioxide [50]. The virtue of 2-carboxyethylgermanium sesquioxide is ascertained with mice to show an anticancer effect to activate macrophages and to produce an interferon [51].

1. $Ge + 3HCl \longrightarrow HGeCl_3 + H_2$

$$HGeCl_3 + CH_2{=}CH\text{-}COOH \longrightarrow Cl_3GeCH_2CH_2COOH$$

$$Cl_3GeCH_2CH_2COOH \xrightarrow[H_2O]{\text{hydrolysis}} (GeCH_2CH_2COOH)_2O_3$$

2. $HGeCl_3 + CH_2{=}CH\text{-}CN \longrightarrow Cl_3GeCH_2CH_2CN$

$$Cl_3GeCH_2CH_2CN \xrightarrow[HCl]{\text{hydrolysis}} Cl_3GeCH_2CH_2COOH$$

3. $HGeCl_3 + CH_2{=}CH\text{-}COCH_3 \longrightarrow Cl_3GeCH_2CH_2COCH_3$

$$Cl_3GeCH_2CH_2COCH_3 \xrightarrow[\text{HCl or } H_2SO_4]{\text{hydrolysis}} (GeCH_2CH_2COCH_3)_2O_3$$

$$(GeCH_2CH_2COCH_3)_2O_3 \xrightarrow[\text{chlorobenzene}]{t\text{-BuOOH, KOH}} (GeCH_2CH_2COOH)_2O_3$$

4. $GeCl_4 + H_2O + H_3PO_2 + CH_2{=}CHCOOH$

$$\longrightarrow Cl_3GeCH_2CH_2COOH + H_3PO_3 + HCl$$

5. $GeCl_4 + H_2O + H_3PO_2 + CH_2{=}CHCONH_2$

$$\longrightarrow Cl_3GeCH_2CH_2CONH_2 + H_3PO_3 + HCl$$

$$Cl_3GeCH_2CH_2CONH_2 \xrightarrow[NaOH]{\text{hydrolysis}} (GeCH_2CH_2COOH)_2O_3$$

6. $GeO_2 + 3HCl + H_3PO_2 \longrightarrow HGeCl_3 + H_3PO_3 + H_2O$

$$HGeCl_3 + CH_2{=}CHCOOH \longrightarrow Cl_3GeCH_2CH_2COOH$$

Scheme 9.2 [35–47]

The 17 patients with rheumatoid arthritis are orally administrated 2-carboxyethylgermanium sesquioxide doses of 1500 mg/day, three times/day for six months and the results are shown in Table 9.4. More than 80% of patients with rheumatic arthritis are improved.

Table 9.4 Effects of a six-month drug exposure to carboxyethylgermanium sesquioxide on 17 patients [52]

Item	Increase	No change	Decrease
peripheral lymphocyte	9 (52.9%)	5 (29.4%)	3 (17.6%)
T cell	9 (52.9%)	6 (35.3%)	2 (11.8%)
B cell	7 (41.2%)	4 (23.5%)	6 (35.3%)
ADCC	10 (58.8%)	5 (29.4%)	2 (11.8%)
NK activity	8 (47.1%)	7 (41.2%)	2 (11.8%)
interferon	15 (88.2%)	2 (11.8%)	4 (23.5%)
RA factor	2 (11.8%)	9 (52.9%)	6 (35.3%)
CRP	0 (0%)	8 (47.1%)	9 (52.9%)

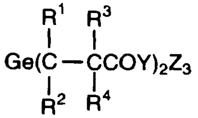
The cause of improvement is considered to be due to stimulation of their immune systems such as interferon, peripheral lymphocyte and T cell. Further, 2-carboxyethylgermanium sesquioxide is also reported as having an immunological modulation effect [53]. Hence, 2-carboxyethylgermanium sesquioxide has been reported that it affects many diseases such as diseases of the nervous system, heart, vascular system, digestive system and skin [41]. Furthermore, 2-carboxyethylgermanium sesquioxide has been developed as a drug for interferon generation enhancing agent [54], immunological enhancing agent [55], drugs for viral and respiratory diseases [45,46,56], AIDS therapeutic agents [57,58], dermatopathy therapeutic agents [23,59–63], morphine-like anodynes [64], anti-hypertensive drugs [47,65], etc. [66].

2-Carboxyethylgermanium sesquioxide, as described above, may be used as a drug for treatments such as antitumor and antivirus because of the action of interferon induction, to activate immunological functions of cells such as T cell. Furthermore, recently it was found that 2-carboxyethylgermanium sesquioxide has the action to inhibit the Maillard reaction. The Maillard reaction is the reaction that bonds excess glucose with protein. It is considered that the accumulation of AGE (Advanced Glycosylation End Products), which is the final product of the Maillard reaction, causes promotion of aging, diabetes complications, for example, cataract, arteriosclerosis, nervous diseases and the decrease in immunity. 2-Carboxyethylgermanium sesquioxide is expected as a drug for these diseases [66a–66g].

Those derivatives (A) with S in place of O, alkyl or allyl derivatives at the methylene group, the ester or amide derivatives, etc. in 2-carboxyethylgermanium sesquioxide have also been synthesized [67–103], and the properties such as anticancer [67,74,76,85,86–94], immunological enhancement [83], the activator of osteoblast [89,90], morphine-like anodyne [71,75,79,80,97], etc. [72,86,88,100], have been found.

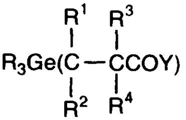
The following similar compounds (B) to 2-carboxyethylgermanium sesquioxide [104–122] are found to show medical properties such as anticancer [107,111–113], morphine-like anodyne [109,110,115] and antibacterial agent [108,120], etc.

Furthermore, those compounds (C) having the cyclized carboxyethylgermanium skeleton [123–125] and other organogermanium compounds [34,126–148] have



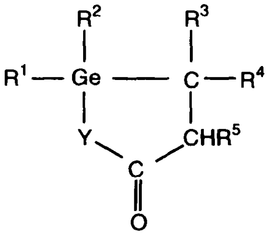
$\mathrm{Ge}(\overset{R^1}{\underset{R^2}{\mathrm{C}}}-\overset{R^3}{\underset{R^4}{\mathrm{C}}}\mathrm{COY})_2\mathrm{Z}_3$ (A)

R^1-R^4 = H, alkyl, aryl, etc.
Z = O, S
Y = OH, OR, OM, NH_2, NR_2,NRR'
R, R' = H, alkyl, aryl, etc.
M = metal atom



$\mathrm{R_3Ge}(\overset{R^1}{\underset{R^2}{\mathrm{C}}}-\overset{R^3}{\underset{R^4}{\mathrm{C}}}\mathrm{COY})$ (B)

R^1-R^4 = H, alkyl, aryl, $NHCOCH_3$, etc.
R = H, alkyl, aryl, halogen
R_3 = $NH(CH_2CH_2O\text{-})_3$, $N(CH_2CH_2S\text{-})_3$
Y = OH, OR', OM, NH_2, NR'_2
R' = alkyl



(C)

R^1-R^6 = H, alkyl, aryl
Y = O, S

been synthesized and developed as drugs such as anticancer [126,127,129,130,133,135, 138,139,141,145,147], anodynes [124], antibacterial agents [137], cancer diagnosis [34], etc.

Dimethylgermanium porphyrin complexes as shown in Figure 9.4 were found to show anticancer activity in rats and mice [149,150].

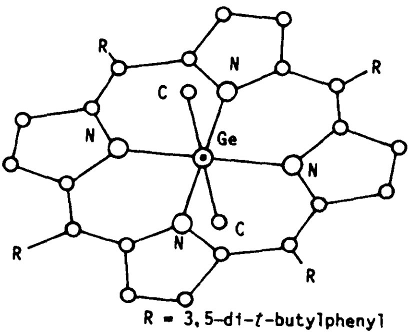
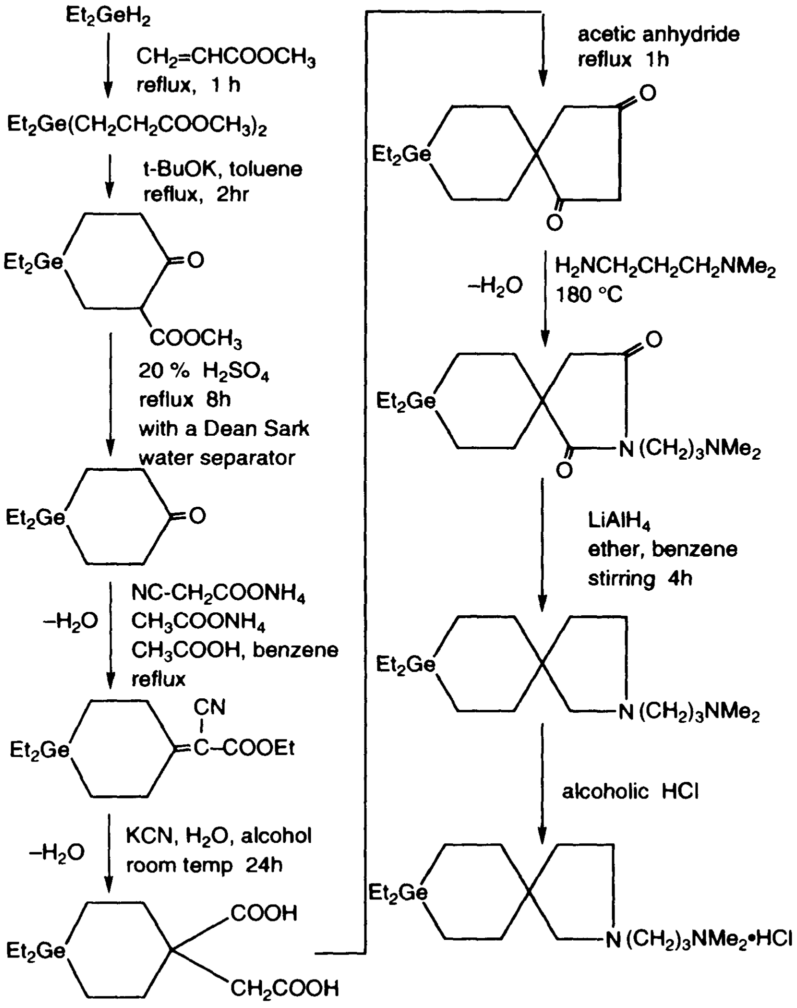


Figure 9.4 Structure of dimethylgermanium porphyrin complex [149].

2-Carboxyethylgermanium sesquioxide described above was synthesized as a compound in 1967 as a water soluble organogermanium compound by Asai and Kakimoto in the Asai Germanium Research Institute as a pharmaceutical substance. In 1979, they initiated clinical trials. Now, even after 18 years, 2-carboxyethylgermanium sesquioxide remains in the phase III state, and it is not approved as a new drug yet. In September 1994, it was approved as a drug for hepatitis B from another company [150a,2a].

As for the other drugs from organogermanium compounds, in the United States, spirogermanium(2-aza-8-germanspiro[4.5]-decane-2-propanamine-8,8-diethyl-N,N-



Scheme 9.3 [153]

Table 9.5 Phase II study of spirogermanium in metastatic prostate cancer patient characteristics and toxic effects [157]

Characteristic	No. of patients
Total	15
Median age in yrs (range): 66 (52–70)	
zubrod performance status	
level 1	9
level 2	5
level 3	1
site of disease	
bone	12
bone and liver	2
bone and skin	1
evaluable patients	15
toxicity and response	13
toxicity only	2
neurologic toxic effects	
blurred vision	9
vertigo	6
confusion	5
hand tremor	5
sensory neuropathy	3
electroencephalogram abnormality	2
headache	1
cogwheel rigidity	1
hearing loss	1
other toxic effects	
hepatic transaminase elevation (2–5 × normal)	4
skin toxicity (hyperkeratosis)	1

dimethyl dihydrochloride is in phase II state [151–157]. This spirogermanium compound is prepared by the process shown in Scheme 9.3 [153]. Phase II study of the spirogermanium compound in metastatic prostate cancer is shown in Table 9.5. The spirogermanium compound was administrated to fifteen patients with metastatic prostate cancer at a dose of $150\,\mathrm{mg/m^2/d}$ for 28 days continuously. Two patients were evaluated only for toxic side effects because they developed severe neurotoxic effects after 4 and 6 days of the treatment. The remaining 13 patients were evaluated for the anticancer responses [157].

Rijkens and van der Kerk [158] have investigated the biological activity of trialkylgermanium on fungi, yeasts and bacteria as shown in Table 9.6. Generally, the antimicrobial activities of organogermanium compounds are slightly less than those of organotin compounds [19,159] and the antimicrobial spectrum is slightly narrower than that of organotin compounds. Many organogermanium compounds seem to be much less toxic to mammals than the corresponding organotin com-

Table 9.6 Antimicrobial activity of triorganogermyl acetates [158]. Minimal concentration (μg/ml) causing complete inhibition of visible growth. Test medium: peptone glucose agar, pH 6.5–7.0

Compounds	fungi					
$R_3GeOOCCH_3$ R	Botrytis allii	Penicillium italicum	Aspergillus niger	Rhizopus nigricans	Glomerella cingulata	Cladosporium cucumerinum
Me	> 500	> 500	> 500	> 500	> 500	> 500
Et	50	200	50	200	10	20
Pr	50	> 500	50	100	5	20
Bu	> 500	> 500	> 500	> 500	10	> 500
Hexyl	> 500	> 500	> 500	> 500	—	—
Ph	> 500	> 500	> 500	> 500	—	—

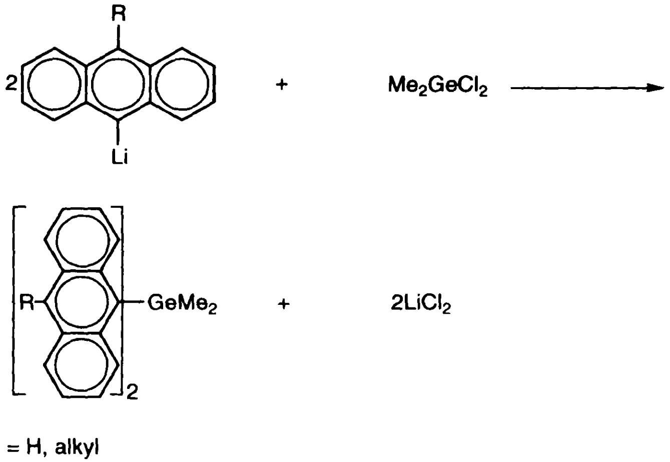
Compounds	bacteria				
	yeast		gram-positive		gram-negative
$R_3GeOOCCH_3$ R	Debaryomyces nicotianae	Saccharomyces cerevisiae	Mycobacterium phlei	Streptococcus lactis	Escherichia coli
Me	200	> 500	> 500	> 500	> 500
Et	2	200	500	50	> 500
Pr	50	200	20	5	> 500
Bu	> 500	> 500	2	1	> 500
Hexyl	—	—	> 500	20	> 500
Ph	> 500	> 500	> 500	> 500	> 500

pounds. Some organogermanium compounds show higher antimicrobial activities to some microbes, e.g., Streptococcus lactis, than those of organotin compounds [158]. Recently, $Me_3GeCH_2CH_2CH_2NHCH_2Ph$ [108] was found to have very high antimicrobial activity with a wide spectrum [108].

9.5.2 OTHERS

Di(9-anthryl)dimethylgermane compound gives a [4 + 2] additive in the benzene solution by light irradiation, and the additive shows a different color. The original compound is regenerated from the additive by heating. The additives are investigated for a rewritable optical disk by taking advantage of this reversibility [160].

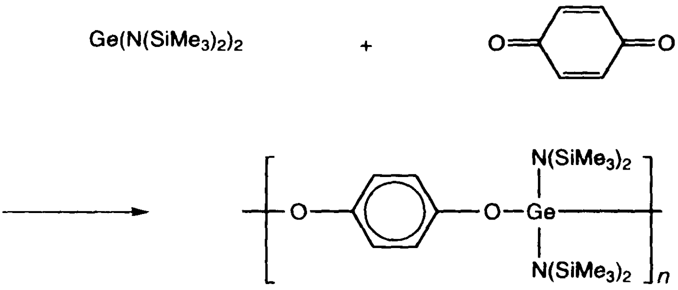
Recently, Asai Germanium Research Institute found that 2-carboxyethylgermanium sesquioxide and its derivatives improve the isomerization of glucose. Usually, the reaction of isomerization of glucose is that glucose is isomerized to fructose by glucoseisomerase. The isomerization ratio with glucoseisomeraze is 42–43 %. With organogermanium compounds, the isomerization ratio increases to 75–92 %, and the product is available as a better sweetening agent without separation of glucose. This process is very hopeful for the production of



(9.10)

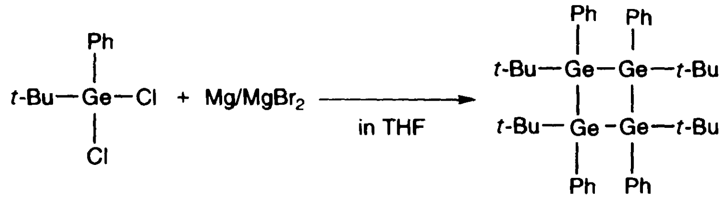
fructose if the recycling technology of organogermanium compounds as catalysts could be found [160a–160c].

Recently, many polymeric compounds and cyclic compounds as shown in eqs. (9.11) and (9.12) have been reported. Divalent organogermanium compounds (germylenes) are liable compounds. However, the handling of the germylene shown in eq. (9.11) is easy. They react with *p*-benzoquinones, cyclic sulfides, cyclic unsaturated carbonyl compounds or acetylenes to give easily the polymers having germanium atoms in the principal chain in high yield [161–165]. The reaction with *p*-benzoquinone is shown in eq. (9.11).



(9.11)

The compound shown in eq. (9.12) has a germanium–germanium bond, that is, it is a polygermane. The polygermanes have just started to develop as new materials having new characteristics similar to polysilanes. The polygermanes are prepared by the reaction of germanium halides with alkali metals or alkaline earth metal [166–168]. The reaction of organogermanium chloride with magnesium and magnesium bromides is shown in eq. (9.12) [166].



(9.12)

major product : *cis-cis-trans*

Finally, organogermanium compounds such as 2-carboxyethylgermanium sesquioxide (Ge-132) has an immunological enhancement action, is known that it prevents and cures some cancers and it is expected to develop drugs for cataract, nervous diseases, arteriosclerosis, kidney diseases, bacterially caused diseases, due to the complication of the promotion of aging and diabetes since it inhibits the Millard reaction. But it is not approved yet in Japan. I hope that it will be approved in the near future, and drugs having no side effects will be developed by investigating the effect of the crude drug such as ginseng and garlic containing germanium compounds.

REFERENCES

[1] E.G. Rochow and E.W. Abel, *The Chemistry of Germanium, Tin and Lead*, Pergamon, Oxford, 1975; F Glockling, *The Chemistry of Germanium*, Academic Press, New York, 1969; V.F. Mironov and T.K. Gar, *Organogermanium Compounds*, Natta, Moscow, 1967.

[1a] *Encyclopedia of Science and Technology, Technopia (Sekai Kagaku Daijiten)*, Kodansha, Tokyo, 1977.

[2] *Kino Zairyo*, September (1990) 47.

[2a] *Kinzoku Jihyo*, No. 1591, p.183, 1995.

[2b] *12695 no Kagaku Shohin*, Kagaku Kogyo Nipposha, Tokyo, 1995.

[2c] *Nikkei Sangyo Shinbun*, July 27, 1995.

[3] Kirk-Othmer, *Concise Encyclopedia of Chemical Technology*, Wiley, New York, 1985.

[4] *Nikkei Sangyo Shinbun*, October 13, 1988.

[5] *Nihon Keizai Shinbun*, October 25, 1987.

[6] *Nihon Keizai Shinbun*, October 8, 1987.

[7] *Nihon Keizai Shinbun*, October 13, 1988.

[8] F. Rijkins, *Organogermanium Compounds*, Germanium Research Committee, 1960.

[9] *Kagaku Daijiten*, Tokyo Kagaku Dojin, p. 870, 1989.

[10] T. Ishiwara, *Z. Krebsforsch.*, **21** (1924) 268.

[11] *Nikkei Sagyo Shinbun*, March 8, 1983.

[12] P. Riviere, M. Riviere-Baudet and J. Satge, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 2, p.399, 1982.

[13] E.G. Rochow, *J. Am. Chem. Soc.*, **69** (1947) 1729.

[14] E.G. Rochow, *J. Am. Chem. Soc.*, **72** (1950) 198.

[15] G. Bähr, H.-O. Kalinowski and S. Pawlenko, *Methoden der Organischen Chemie, Metallorganische Verbindungen*, E. Müller and O. Bayer ed., Houben-Weyl, Band XIII/6, p.1, 1978.
[16] L.M. Dennis and F.E. Hance, *J. Phys. Chem.*, **30** (1925) 1055.
[17] A.K. Fischer, R.C. West and E.G. Rochow, *J. Am. Chem. Soc.*, **16** (1954) 5878.
[18] S. Pawlenko, *Organosilicon Chemistry*, Walter de Gruyter, Berlin, 1986.
[19] I. Omae, *Organotin Chemistry*, *J. Organomet. Chem. Lib. 21*, Elsevier, Amsterdam, 1989.
[20] M. Lesbre, P. Mazerolles and J. Satge, *The Organic Compounds of Germanium*, Wiley, London, 1971.
[21] *Japan Patent Kokai*, 61-205216 (1986).
[22] *Japan Patent*, 46-2964 (1971).
[23] *Japan Patent Kokai*, 62-111908 (1987).
[24] *Japan Patent Kokai*, 61-216625 (1986).
[25] *Japan Patent*, 62-12797 (1987).
[26] *Japan Patent*, 55-32716 (1980).
[27] *Japan Patent Kokai*, 63-17891 (1988).
[28] *Japan Patent Kokai*, 62-230795 (1987).
[29] *Japan Patent Kokai*, 63-17889 (1988).
[30] *Japan Patent Kokai*, 63-17890 (1988).
[31] *Japan Patent Kokai*, 63-77888 (1988).
[32] *Japan Patent Kokai*, 59-227889 (1984).
[33] *Japan Patent*, 59-38927 (1984).
[34] *Japan Patent Kokai*, 63-104987 (1988).
[35] *Japan Patent*, 46-2498 (1971).
[36] M. Tsutsui, N. Kakimoto, D.D. Axtell, H. Oikawa and K. Asai, *J. Am. Chem. Soc.*, **98** (1976) 8287.
[37] *Japan Patent Kokai*, 61-5087 (1985).
[38] *Japan Patent Kokai*, 61-87688 (1986).
[39] *Japan Patent Kokai*, 62-283985 (1987).
[40] *Japan Patent Kokai*, 59-184193 (1984).
[41] *Japan Patent*, 57-53800 (1982).
[42] *Japan Patent*, 53-7960 (1978).
[42a] *Japan Patent*, 59-40159 (1984).
[43] *Japan Patent*, 59-45677 (1984).
[44] *Japan Patent*, 63-62492 (1988).
[45] *Japan Patent*, 63-62493 (1988).
[46] *Japan Patent*, 63-62495 (1988).
[47] *Japan Patent*, 1-24767 (1989).
[48] N. Kumano, Y. Nakai, T. Ishikawa, S. Koinumaru, S. Suzuki and K. Konno, *Sci. Rep. Res. Inst. Tohoku Univ. C*, vol.25, Nos. 3–4, (1978)89.
[49] *Japan Patent Kokai*, 60-190714 (1985).
[50] *Japan Patent Kokai*, 62-252794 (1987).
[51] H. Masho, T. Yamaguchi, K. Nakata, T. Ebina and N. Ishida, *Nihon Gan Gakkai Sokai Kiji*, **39** (1980) 87.
[52] S. Arimori and M. Yoshida, *Igaku to Seibutsu* **104**(4) (1982) 211.
[53] Y. Mizushima and Y. Syoji, *Igaku no Ayumi* **114**(13) (1980) 1055.
[54] *Japan Patent Kokai*, 2-134318 (1990).
[55] *Japan Patent Kokai*, 1-139587 (1989).
[56] *Japan Patent Kokai*, 61-145115 (1986).
[57] *Japan Patent Kokai*, 63-307821 (1988).
[58] *Japan Patent Kokai*, 2-145517 (1990).
[59] *Japan Patent Kokai*, 61-263458 (1986).

[60] *Japan Patent Kokai*, 62-29521 (1987).

[61] *Japan Patent Kokai*, 62-161724 (1987).

[62] *Japan Patent Kokai*, 63-313727 (1988).

[63] *Japan Patent*, 63-61288 (1988).

[64] *Japan Patent*, 61-58447 (1986).

[65] *Japan Patent Kokai*, 63-230695 (1988).

[66] *Japan Patent Kokai*, 1-193218 (1989).

[66a] M. Akiba and N. Kakimoto, *Nihon Kagakukaishi*, (1994) 286.

[66b] K. Nakamura, K. Nomoto, T. Osawa, Y. Takahahsi, M. Akiba, and N. Kakimoto, *Nihon Kagakukaishi*, (1994) 307.

[66c] T. Osawa, S. Kawakishi, M. Akiba and N. Kakimoto, *Main Group Metal Chemistry*, **17** (1994) 251.

[66d] K. Nakamura, K. Nomoto, K. Kariya, Y. Nakajima, H. Nishimoto, S. Ugo, M. Miyata, T. Osawa, S. Kawakishi and N. Kakimoto, *Amino Acid*, **1** (1991) 263.

[66e] F. Hayase, *Kagaku to Seibutsu*, **31** (1993) 592.

[66f] N. Kakimoto, K. Miyano and M. Akiba, *Frontiers of Organogermanium, Tin and Lead Chemistry*, Riga, p.319, 1993.

[66g] T. Osawa, S. Kawakishi, N. Kakimoto and M. Akiba, *Todai Symposium, Ge-Sn-Pb, Tokyo, 1993*, LB302, p.37, 1993.

[67] *Japan Patent Kokai*, 62-252794 (1987).

[68] *Japan Patent Kokai*, 59-216894 (1984).

[69] *Japan Patent Kokai*, 59-141586 (1984).

[70] *Japan Patent*, 59-35916 (1984).

[71] *Japan Patent Kokai*, 60-16997 (1985).

[72] *Japan Patent Kokai*, 60-226592 (1985).

[73] *Japan Patent*, 62-18590 (1987).

[74] *Japan Patent*, 61-58448 (1986).

[75] *Japan Patent Kokai*, 59-78197 (1984).

[76] *Japan Patent Kokai*, 61-65819 (1986).

[77] *Japan Patent Kokai*, 62-142189 (1987).

[78] *Japan Patent Kokai*, 62-252793 (1987).

[79] *Japan Patent Kokai*, 62-93293 (1987).

[80] *Japan Patent Kokai*, 61-112087 (1986).

[81] *Japan Patent Kokai*, 63-316792 (1988).

[82] *Japan Patent Kokai*, 64-3191 (1989).

[83] *Japan Patent Kokai*, 61-151123 (1986).

[84] *Japan Patent Kokai*, 61-148186 (1986).

[85] *Japan Patent Kokai*, 59-76095 (1984).

[86] *Japan Patent Kokai*, 59-36686 (1984).

[87] *Japan Patent Kokai*, 59-141587 (1984).

[88] *Japan Patent Kokai*, 61-145116 (1986).

[89] *Japan Patent Kokai*, 1-149723 (1989).

[90] *Japan Patent Kokai*, 63-107920 (1988).

[91] *Japan Patent Kokai*, 63-211226 (1988).

[92] *Japan Patent Kokai*, 59-225117 (1984).

[93] *Japan Patent Kokai*, 62-187409 (1987).

[94] *Japan Patent Kokai*, 59-33292 (1984).

[95] *Japan Patent Kokai*, 60-41685 (1985).

[96] *Japan Patent*, 59-36998 (1984).

[97] *Japan Patent Kokai*, 60-12981 (1985).

[98] *Japan Patent*, 62-24438 (1987).

[99] *Japan Patent*, 62-28797 (1987).

[100] *Japan Patent*, 63-28070 (1988).

[101] *Japan Patent*, 59-35917 (1984).
[102] *Japan Patent*, 59-36997 (1984).
[103] N. Kakimoto, M. Akiba and T. Takada. *Synthesis*, March (1985) 272.
[104] *Japan Patent Kokai*, 61-148185 (1986).
[105] *Japan Patent Kokai*, 62-92 (1987).
[106] *Japan Patent Kokai*, 62-174089 (1987).
[107] *Japan Patent Kokai*, 59-216893 (1984).
[108] *Japan Patent Kokai*, 62-93 (1987).
[109] *Japan Patent Kokai*, 62-228014 (1987).
[110] *Japan Patent Kokai*, 62-175176 (1987).
[111] *Japan Patent Kokai*, 62-158211 (1987).
[112] *Japan Patent Kokai*, 62-158212 (1987).
[113] *Japan Patent Kokai*, 59-31784 (1984).
[114] *Japan Patent Kokai*, 2-62885 (1990).
[115] *Japan Patent Kokai*, 61-158989 (1986).
[116] *Japan Patent Kokai*, 60-246391 (1985).
[117] *Japan Patent Kokai*, 2-200690 (1990).
[118] *Japan Patent*, 61-57319 (1986).
[119] *Japan Patent*, 60-23676 (1985).
[120] *Japan Patent*, 61-13684 (1986).
[121] *Japan Patent*, 59-23319 (1984).
[122] *Japan Patent*, 59-18399 (1984).
[123] N. Kakimoto, T. Yoshiwara, M. Akiba and Y. Ishido, *J. Organomet. Chem.*, **385** (1990) 247.
[124] *Japan Patent Kokai*, 61-267591 (1986).
[125] *Japan Patent Kokai*, 2-78689 (1990).
[126] *Japan Patent Kokai*, 60-1191 (1985).
[127] *Japan Patent Kokai*, 60-100588 (1985).
[128] *Japan Patent Kokai*, 60-11494 (1985).
[129] *Japan Patent Kokai*, 59-31785 (1984).
[130] *Japan Patent Kokai*, 60-1192 (1985).
[131] *Japan Patent Kokai*, 61-100588 (1986).
[132] *Japan Patent Kokai*, 60-84295 (1985).
[133] *Japan Patent Kokai*, 60-228490 (1985).
[134] *Japan Patent Kokai*, 59-95293 (1984).
[135] *Japan Patent Kokai*, 59-193897 (1984).
[136] *Japan Patent Kokai*, 1-249783 (1989).
[137] *Japan Patent Kokai*, 2-131490 (1990).
[138] *Japan Patent*, 57-11916 (1982).
[139] *Japan Patent*, 61-38199 (1986).
[140] *Japan Patent*, 62-7915 (1987).
[141] *Japan Patent*, 59-35918 (1984).
[142] *Japan Patent*, 63-4549 (1988).
[143] *Japan Patent*, 63-4550 (1988).
[144] *Japan Patent*, 63-6076 (1988).
[145] *Japan Patent*, 63-32360 (1988).
[146] *Japan Patent*, 63-38034 (1988).
[147] *Japan Patent*, 57-20315 (1982).
[148] *Japan Patent*, 63-7192 (1988).
[149] *Gendai Kagaku*, October (1983) 9.
[150] S. Shimada, M. Kumakura, O. Yano, E. Kuramoto and T. Iwata, *Koseisho Shinyaku Kaihatsu Suishinkaigi Kinzokusakutai Kenkyuhan Showa 55-59-nendo Kenkyu Houkoku* p. 144.

[151] O. Wada, H. Yanagisawa and Y. Kitagawa, *Bunseki*, (1988) 322.

[152] C.M. Riley, E.A. Monnot, J.F. Stobaugh and M. Slavik, *J. Pharm. Biomed. Anal.*, **7** (1989) 385.

[153] L.M. Rice, J.W. Wheeler and C.F. Geschickter, *J. Hetrocycl. Chem.*, **11** (1974) 1041.

[154] P.S. Schein, M. Slavik, T. Smythe, D. Hoth, F. Smith, J.S. Macdonald and P.V. Woolley, *Cancer, Treatment Reports*, **64** (1980) 1051.

[155] B.T. Hill, S.A. Whatley, A.S. Bellamy, L.Y. Jenkins and D.H. Whelan, *Cancer Research*, **42** (1982) 2852.

[156] A.M. Badger, C.K. Mirabelli and M. DiMartino, *Immunopharmacology*, **10** (1985) 201.

[157] F.H. Dexeus, C. Logothetis, M.L. Samuels and B. Hossan, *Cancer Treatment Reports*, **70** (1986) 1129.

[158] F. Rijkens and G.J.M. van der Kerk, *Organogermanium Chemistry*, Germanium Research Committee, 1964.

[159] G.J.M. van der Kerk and J.G.A. Luijten, *J. Appl. Chem.*, **4** (1954) 314.

[160] *Japan Patent Kokai*, 61-205290 (1986).

[160a] T. Kasumi, N. Kakimoto, M. Akiba, S. Mori, S. Ichikawa and K. Umeda, *8th Int. Conf. on Organometallic Chemistry of Ge, Sn and Pb., September 17, 1995.*

[160b] T. Harumi, S. Ri, S. Ichikawa, N. Kakimoto and K. Umeda, *Shokuhin Kagaku Kougakkai*, March, 1995.

[160c] *Shokuhin Kagaku Shinbun*, December 21, 1995.

[161] S. Kobayashi and S. Shoda, *Nihon Kagakukaishi*, (1994)280.

[162] I. Tomita and T. Endo, *Kobunshi*, **42** (1993) 572.

[163] S. Kobayashi, S. Iwata, K. Yajima, K. Yagi and S. Shoda, *J. Am. Chem. Soc.*, **114** (1992) 4929.

[164] S. Kobayashi, S. Iwata and M. Hiraishi, *J. Am. Chem. Soc.*, **116** (1994) 6047.

[165] S. Kobayshi, S. Iwata, M. Abe and S. Shoda, *J. Am. Chem. Soc.*, **117** (1995) 2187.

[166] A. Sekiguchi, T. Yatabe, H. Naito, C. Kabuto and H. Sakurai, *Chem. Lett.*, (1992) 1697.

[167] K. Mochida, *Nihon Kagakukaishi*, (1994)224.

[168] A. Sekiguchi, H. Naito, C. Kabuto and H. Sakurai, *Nihon Kagakukaishi*, (1994) 248.

10 Organotin Compounds

10.1 INTRODUCTION

Organotin compounds have a long history among the organometallic compounds as described in Chapter 2. Of the metals used as organometallic compounds, tin is a low price metal, since tin is a metal for general uses. Therefore organotin compounds are easily prepared at a relatively low price. Organotin compounds are one of those organometallic compounds used in large quantities since they have various kinds of characteristics. Hence, the chapter mainly describes their uses, and only briefly describes their preparations, reactions and structures. Please refer to books and reviews for further details [1–5].

10.2 TIN

Tin belongs to the group 14 element, the same as carbon, with an outer electron structure of $5s^25p^2$. Tin exists as 2.2 ppm in the Earth's crust [6]. About 200×10^3 tons per year is produced in the world [7].

In the production of tin, the major ore is cassiterite (tinstone), for which the specific gravity is large, about 7. Therefore the concentrate is obtained with ore dressing by gravity separation. The reduction of the concentrate with coke or anthracite in the reverberating furnace, electric furnace or smelting furnace gives a crude tin. The crude tin contains small amounts of Cu, Pb, Sb, Bi, Fe, As, etc. Pure tin is prepared by electrolysis refining with hexafluorosilicate (H_2SiF_6) as electrolyte.

The properties of tin is shown in Table 10.1 [1]. The valence number is 2 or 4. Valence 2 is always positive; however, valence 4 has amphoteric properties showing $+4$ or -4 according to its reaction partner. The metal has at least two allotropic modifications, i.e., the α- and β-forms. White tin, which is usually seen, is the β-tin. The transformation temperature from white to gray α-tin is 13.2 °C. The transformation rate increases as the temperature decreases, and reaches a maximum at -48 °C. The small amounts of Bi, Sb, Pb, Ag and Au in the tin retard the transformation. Thus, commercial grade tin resists the transformation because of the inhibiting effect of these elements which are present as impurities. Tin is inert and does not react with air and water at ordinary temperatures. But at high temperatures it forms a very thin oxide layer on the surface. In oxygen, tin hardly shows any reactivity at ordinary temperatures. However, when tin is heated in

Table 10.1 Properties of tin [1]

Property	Value
melting point, °C	231.9
boiling point, °C	2625
crystal structure	tetragonal crystal system
transformation temperature:	
α-form to β-form, (°C)	13.2
density, g/cm^3	
α-form (gray tin)	5.77
β-form (white tin)	7.29
linear coefficient of thermal expansion at 0°C, K^{-1}	0.199×10^{-4}
electrical resistivity, μΩ·cm	11.4
Brinell hardness (10kg, 5mm, 180s, at 20°C)	3.9
thermal conductivity, cal.cm^{-1}.S^{-1}.deg^{-1}, at 20°C	0.155
magnetic susceptibility, 18°C	0.027×10^{-6}
ionic radius	
Sn^{2+}, nm	0.093
Sn^{4+}, nm	0.074
covalent radius, single bond, nm	0.140

oxygen, it burns with a pale white flame to yield tin oxide. Chlorine, bromine, and iodine react with tin at normal temperatures, and fluorine reacts at 100°C forming the appropriate stannic halides. When tin is mixed with sulfur, selenium or tellurium and heated, it reacts violently [1]. Tin has an amphoteric nature since it reacts with strong acids and strong bases. Metallic tin is attacked by hydrogen halides and it is dissolved by a hot aqueous solution of alkali hydroxide to form an alkaline stannite and hydrogen. Dry hydrogen sulfide does not react with tin at ordinary temperatures; however, at 100–400°C, the reaction proceeds easily to yield stannous sulfide. Phosphorus pentachloride reacts with fine powdery tin at 170°C to give stannic chloride and phosphorus trichloride (PCl_3) [1].

10.3 PREPARATION OF ORGANOTIN COMPOUNDS

Organotin compounds are prepared by the following four reactions:

(1) Grignard reactions
(2) Wurtz reactions
(3) Reactions with organoaluminum compounds
(4) Direct reactions

In these reactions, Grignard reactions, Wurtz reactions and reactions with aluminum compounds are available for the synthesis of R_4Sn. The direct reactions are available for the synthesis of R_2SnX_2. The industrial preparation of various kinds of organotin compounds are performed not by one process but by all of these reactions because the reactivity of each organic residue is different. In these reaction processes, the number of preparation examples of the Wurtz reaction are relatively few and the use of this process is restricted in the countries within Eastern Europe.

10.3.1 GRIGNARD REACTIONS

The Grignard reaction is widely used both experimentally and industrially. This is probably because the Grignard reaction easily gives R_4Sn in a high yield with excess Grignard reagent, and other organotin derivatives are produced by a redistribution reaction (Kocheskov reaction) as shown in eqs. (10.2)–(10.4).

$$4RMgX + SnX_4 \longrightarrow R_4Sn + 4MgX_2 \tag{10.1}$$

$$3R_4Sn + SnCl_4 \longrightarrow 4R_3SnCl \tag{10.2}$$

$$R_4Sn + SnCl_4 \longrightarrow 2R_2SnCl_2 \tag{10.3}$$

$$R_4Sn + 3SnCl_4 \longrightarrow 4RSnCl_3 \tag{10.4}$$

In the Grignard reactions, a four-fold excess of Grignard reagent as an alkylating agent over stannic halides is theoretically required as shown in eq. (10.1). But actually, the resulting product is a mixture of R_4Sn, R_3SnX, R_2SnX_2 and $RSnX_3$ when the four molar ratio of Grignard reagent to SnX_4 is used. So, generally, by using more than the four molar ratio of Grignard reagent to SnX_4, the Grignard reaction can be used to prepare only tetraorganotin (R_4Sn). To obtain R_nSnX_{4-n} ($n = 1$–3) from R_4Sn requires one to carry out the distribution reaction (about 200 °C, for several hours) as shown in eqs. (10.2)–(10.4). The resulting product contains a higher ratio of the mixture of R_3SnX, R_2SnX_2 and $RSnX_3$ compared with R_4Sn when less than the four-fold ratio of Grignard reagents to SnX_4 is used. Thus the Grignard reaction is an unattractive method for the preparation of organotin halides (R_nSnX_{4-n}, $n = 1$–3) directly.

Chlorinated or brominated hydrocarbons are usually used as the starting materials. On the other hand, iodides are rarely used because of the low yield.

The conventional solvent for the Grignard reaction is ethyl ether or an ethyl ether-hydrocarbon mixture. But recently tetrahydrofuran and butyl ether have been found to be good solvents and they give improved yields.

Grignard reactions are of wide applicability for a great range of organic groups, but steric hindrance affect these reactions considerably, and yields from the compound having a secondary or tertiary aliphatic group and long chain alkyl, phenyl or vinyl groups are poor.

10.3.2 WURTZ REACTIONS

The Wurtz reaction is the reaction with sodium metal as shown in eq. (10.5). One disadvantage is that large volumes of solvent have to be used to suppress the conversion of an alkyl chloride RCl to a hydrocarbon R–R. Moreover, R_2Sn, R_3SnSnR_3, SnX_2 and R–R are by-products which are difficult to be converted economically to the desired products. The yields are lower than those of the Grignard reaction. The Wurtz reaction is applied mainly for the reactions of simple alkyl chlorides or aryl chlorides [1].

$$SnX_4 + 4RX + 8Na \longrightarrow R_4Sn + 8NaX \quad (10.5)$$

10.3.3 REACTIONS WITH ORGANOALUMINUM COMPOUNDS

Organotin compounds are prepared by reaction with organoaluminum compounds as shown in eq. (10.6). The reaction yields AlX_3. The AlX_3 easily form the complex ($R_nSnX_{4-n}{\cdot}AlX_3$, $n = 1$–3) with R_nSnX_{4-n}. Therefore the formation of the complex lowers the yields of R_4Sn. Hence, this reaction requires a stronger complexing agent for the further alkylation of R_nSnX_{4-n} to proceed easily in the presence of AlX_3. Ether, amines and sodium chloride are available as the complexing agent. For example, the reaction with an ether is shown in eq. (10.7) [1].

$$4R_3Al + 3SnX_4 \longrightarrow 3R_4Sn + 4AlX_3 \quad (10.6)$$

$$4R_3Al + 3SnCl_4 + 4R'_2O \longrightarrow 3R_4Sn + 4Cl_3AlOR'_2 \quad (10.7)$$

Alkylation with an organoaluminum compound has the advantage that it can be carried out in the absence of the solvent, and tetrabutyltin and tetraoctyltin are prepared industrially by this method [1].

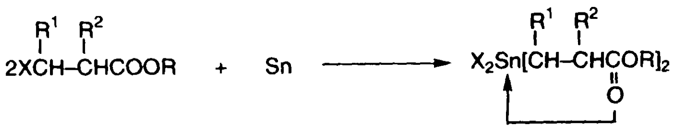
10.3.4 DIRECT REACTIONS

The direct reaction is the reaction found by Frankland in 1849.

$$2RX + Sn \longrightarrow R_2SnX_2 \quad (10.8)$$

The order of reactivity of the alkyl halides is $RI > RBr > RCl$, and for a given halogen, $MeX > EtX > PrX$, etc. Sumio Matsuda and Haruo Matsuda in Osaka University found that magnesium and butanol, etc. are excellent catalysts for this reaction in 1960 as shown in eq. (10.9) [8–14]. Esters, ketones and amines easily react with tin in the presence of these catalysts and organotin compounds having a functional group are prepared in a high yield [14–34g]. The reaction with esters is shown in eq. (10.10) [1,24].

$$2BuI + Sn \xrightarrow[130-135\ ^\circ C,\ 3\ hr]{Mg,\ BuOH} \underset{92\text{-}95\ \%}{Bu_2SnI_2} \qquad (10.9)$$



$$2X\overset{R^1}{\underset{|}{C}}H-\overset{R^2}{\underset{|}{C}}HCOOR + Sn \longrightarrow X_2Sn[\overset{R^1}{C}H-\overset{R^2}{C}H\underset{O}{\overset{\|}{C}}OR]_2 \qquad (10.10)$$

10.4 REACTION OF ORGANOTIN COMPOUNDS

The reactions of organotin compounds are: Kocheskov reaction shown in eqs. (10.2)–(10.4) described above and the following five reactions:

(1) Hydrostannation
(2) Hydrostannolysis
(3) Triorganotin radical reactions
(4) Organostannylene reactions
(5) Others

10.4.1 HYDROSTANNATION

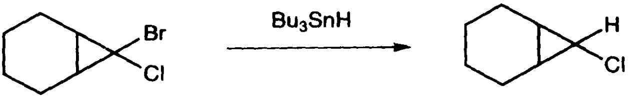
Hydrostannation is a reaction of hydrometalation such as hydrosilylation, hydrogermylation and hydroboration described in the previous chapters. It is a reaction of unsaturated compounds such as olefins and acetylenes with tin hydride. In particular, hydrostannation readily gives a compound having a functional group substituted by organotins in the reaction of a compound having a carbon–carbon unsaturated bond containing a functional group and the tin atom is almost exclusively attached to the terminal carbon. It is well known that the radical derived from a terminal addition ($R_3Sn\dot{C}H_2C(H)R'$, $R' = COOMe$) is more stable than that of non-terminal addition ($R_3SnCHR'CH_2\cdot$), since here the substituent R′ participates in the resonance stabilization of the former structure [1].

$$Me_3SnH + CH_2{=}CR'COOMe \longrightarrow Me_3SnCH_2CHR'COOMe \qquad (10.11)$$

In hydrostannation, not only carbon–carbon unsaturated compounds but also compounds having C=O, C=N, N=N, N=C=S, N=C=O, etc. are used as the unsaturated compounds [1].

10.4.2 HYDROSTANNOLYSIS

Hydrostannolysis is usually a reaction in which the bond between alkyl (or aryl) group and halogen or sulfur is cleaved reductively by an organotin hydride. In particular, hydrostannolysis is available for the dehalogenation reaction of a halide as shown in eq. (10.12). This reduction usually occurs in a stepwise fashion, the



(10.12)

dehalogenation of two halogens requires two times the amount of tin hydride. Hydrostannolysis usually occurs in high yields under mild reaction conditions. This reaction is considered to proceed with a free-radical mechanism [1].

10.4.3 TRIORGANOTIN RADICAL REACTIONS

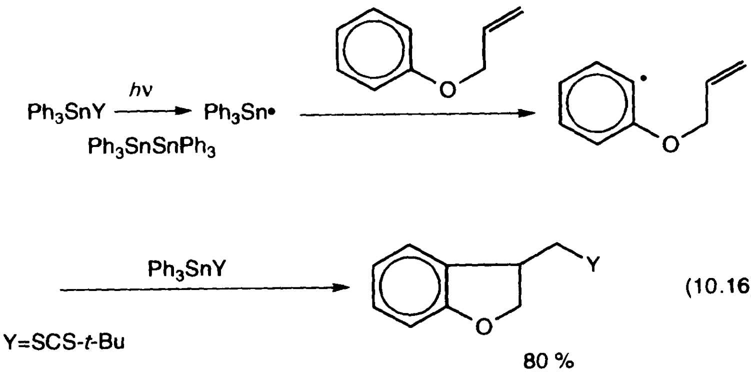
The dissociation energy of Me_3C-H and Me_3C-CH_3 are 104 and 82kcal/mol, respectively, whereas the dissociation energy of Me_3Sn-H, Me_3Sn-CH_3 and $Me_3Sn-SnMe_3$ are 70, 65 and 63kcal/mol, respectively and the bonds of R_3Sn-CH_3 and $R_3Sn-SnR_3$ are weak. Therefore, by light irradiation or in the presence of radical initiators, these compounds yield easily $R_3Sn\cdot$ as shown in eqs. (10.13) and (10.14) [1]. $R_3Sn\cdot$ formed, is available for the radical reaction as the radical source.

$$R_3SnSnR_3 \xrightarrow{h\nu} 2R_3Sn\bullet \qquad (10.13)$$

$$t\text{-BiO}\bullet + R_3SnSnR_3 \longrightarrow BuOSnR_3 + R_3Sn\bullet \qquad (10.14)$$

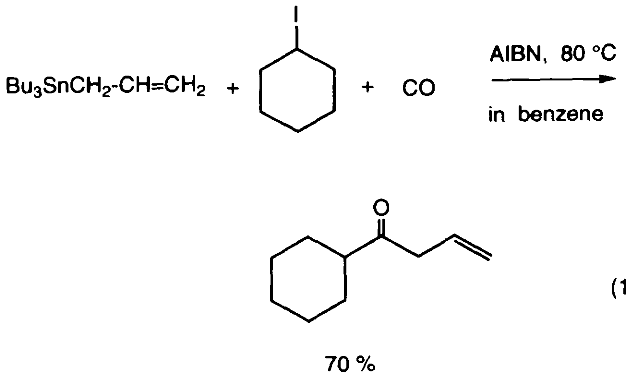
The reaction with halides yields a new R· radical as shown in eq. (10.15). For example, as shown in eq. (10.16), the reactions are available for a cyclization [35].

$$R_3Sn\bullet + R'X \longrightarrow R_3SnX + R'\bullet \qquad (10.15)$$



(10.16)

On the other hand, trialkyltin compound reacts with a halide in the presence of carbon monoxide to give an allylketone by a carbonylation as shown in eq. (10.17) [36].



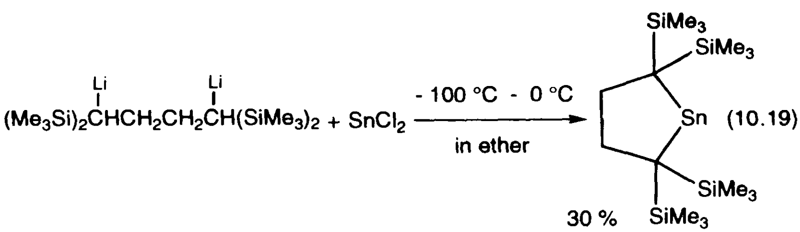
(10.17)

10.4.4 REACTIONS OF ORGANOSTANNYLENES

Divalent organotin compounds (organostannylenes) represented by R_2Sn and the compounds of which R is alkyl or aryl, are liable. But the organic groups shown in eqs. (10.18)–(10.20) are stably obtained [37–40]. The compound shown in eq. (10.18) has a three-coordination structure of dimer ($((Me_3Si)_2CH)_2Sn$-$Sn(CH(SiMe_3)_2)_2$). On the other hand, the compounds shown in eq. (10.20) is four coordination with the coordination of pyridine.

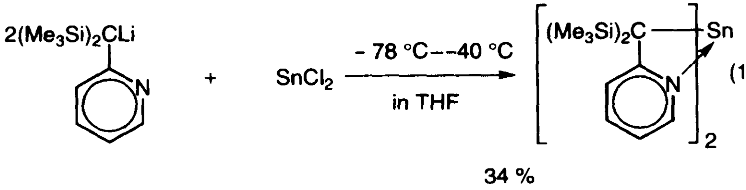
$$2(Me_3Si)_2CHLi + SnCl_2 \xrightarrow[\text{in ether}]{0\ °C} ((Me_3Si)_2CH)_2Sn \qquad (10.18)$$

54 %



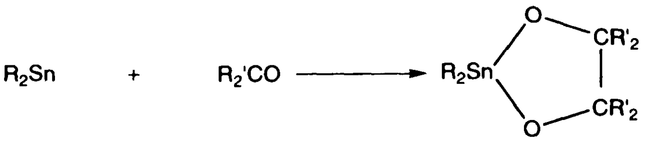
(10.19)

Organostannylenes are reactive compounds and an insertion (oxidative addition) and a cyclization tend to proceed, and tend to polymerize by themselves. For example, insertion and cyclization reactions are shown in eqs. (10.21) and (10.22), respectively [1].



(10.20)

$$R_2Sn + Me_3SnSnMe_3 \longrightarrow R_2Sn(SnMe_3)_2 \qquad (10.21)$$



(10.22)

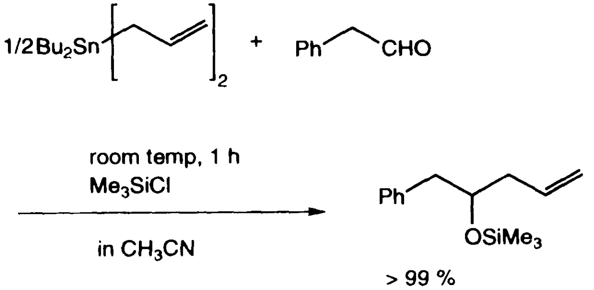
10.4.5 OTHERS

The other reaction is organostannolysis. Organostannolysis is the reaction with organic groups in place of hydrogen of hydrostannolysis described in Section 10.4.2. The reaction is shown in eq. (10.22a). These types of reaction are an

$$R'_3SnY + RZ \longrightarrow RY + R'_3SnZ \qquad (10.22a)$$

$Y = CH_2\text{-}CH{=}CH_2$, $CH{=}CR''_2$, $C{\equiv}CR''$, $R''CH_2Ph$, Ph, etc.

allylation, vinylation, alkynylation, alkylation, benzylation, arylation, etc. with organotin compounds. These are the organosynthetic reactions with organotin compounds. Recently, many articles have been published. Please refer to *Organotin Chemistry* published in 1989 [1]. Trialkyltin compounds are usually used in these reactions. However, a few examples with dialkyltin compounds are shown in eq. (10.22b) [40a].



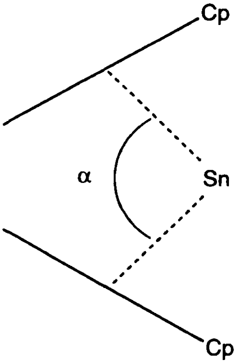
(10.22b)

10.5 STRUCTURE OF ORGANOTIN COMPOUNDS

Organotin compounds are divalent (Sn(II)) and tetravalent (Sn(IV)) and the coordination numbers of 2, 3, 4, 5, 6 and 7 are known. The 3, 4, 5, 6 and 7 coordination correspond to trigonal, tetrahedral, trigonal bipyramidal, octahedral and pentagonal bipyramidal structures, respectively.

Organostannylenes tend to polymerize as described above [41]. But the compounds bonded with a bulky group form a dimer of a three-coordination type compound (e.g., $((Me_3Si)_2CH)_2SnSn(CH(SiMe_3)_2)_2)$ shown in eq. (10.18)). On the other hand, the compound shown in eq. (10.20) can form a four-coordination type compound by intramolecular coordination. However, the divalent two-coordination type compound shown in eq. (10.19) forms not a linear but a bent structure. Stannocene also has the bent structure as shown in Figure 10.1 [42–46]. Generally, the Sn-ring centroid angle becomes larger when the more bulky substituents are present. Stannocene bonded with five phenyl groups to each cyclopentadienyl ring is parallel (180°).

As organostannylenes have an active lone pair of electrons (R_2Sn:), they form the complex to strong Lewis acids such as BF_3 ($R_2Sn \rightarrow BF_3$). For example, the reaction with $Cr(CO)_6$ gives $((Me_3Si)_2CH)_2SnCr(CO)_5$. $((Me_3Si)_2CH)_2SnCr(CO)_5$ has a planar three coordination. The bond between Sn and Cr is considered to be a π-interaction between the 3d orbital of Cr atom with vacant 5p or 5d orbital of tin atom.

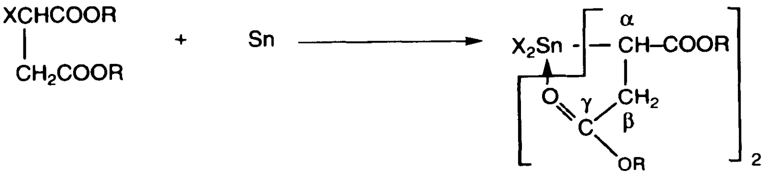


Substituent of Cp	CpSnCp (α)
H	145.9 °
1,2,3,4,5-Me	144.1 °
1,2,4-$SiMe_3$	162°
1,2,4-i-Pr	165.0 °
1,2,3,4,5-Ph	180°

Figure 10.1 Structure of stannocenes and the Sn-ring centroid angles [42–46]

The Cr–Sn bond length of $(CO)_3CpCr-SnPh_3$ is 2.85 Å. However, the Cr–Sn bond length of $((Me_3Si)_2CH)_2Sn-Cr(CO)_5$ is 2.562 Å. The latter is very short and this bond is considered to be a carbene complex (Sn=Cr) [47,48].

The author and his coworkers at Osaka University tried the direct reactions of the compound having a functional group such as a haloester (eq. (10.10)), haloketone and haloamide with tin metal. In these reactions, the structure of the reaction products of halodicarboxylic acid ester with tin as shown in eq. (10.23) are



(10.23)

X	R	m.p. (°C)	
Br	Me	130-131,	157.5-158.5
Br	Et	114-115,	122-123
I	Me	-	164.5-165.5
I	Et	99-101,	118.5-119.5
I	*n*-Pr	-	77-78

investigated by their IR and NMR spectra. The author found large shifts in these spectra, and presumed that the shifts are caused by the intramolecular coordination [16]. Afterwards he established the structure of X-ray diffraction studies [20,23]. He pointed out that these intramolecular coordinations are the coordination of O, S and N atom bonded to the carbon at the γ-position. He pointed out that these compounds are very easily produced and the products having five-membered rings are very stable. In their laboratories, the specificity of the ring structure was called the five-membered ring structure theory. The specificity of the five-membered ring is not only for organotin compounds but also almost all organometallic compounds. In many organometallic compounds, the author compiled intermolecular coordination compounds having mainly five-membered ring structures in 1986 and he published it in a book form entitled *Organometallic Intramolecular-coordination Compounds* from Elsevier [49].

In 1995, at the 69th Annual Spring Meeting of the Chemical Society of Japan, he presented the result that strain energies for the cyclic structures of alkoxycarbonylalkyltin trichlorides are calculated by utilizing the MM2 force field, Dreiding force field in molecular force field method, and PM3 semiempirical molecular orbital method. The results show that the orders of stability in these ring systems are five-membered ring > six-membered ring by MM2 method, five- > six- > seven- > four-membered ring by Dreiding method, and five- > six- > four-membered ring by PM3 semiempirical molecular orbital method [50]. Furthermore the results calculated by using an *ab initio* molecular orbital method show the same order as those calculated by the PM3 method [50a]. All these calculation methods show that the five-membered ring is the most stable.

10.6 APPLICATIONS OF ORGANOTIN COMPOUNDS

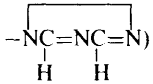
International Tin Research Institute (Int. Tin Res. Inst.) is an international research institute on tin. This institute was established in 1932 in England for expanding the effective uses of tin by the five tin producing countries of Indonesia, Malaysia, Nigeria, Thailand and Zaire. Recently, the Int. Tin Res. Inst. has changed to the company called "Int. Tin Res. Inst. Limited" supported by tin producing companies. The former Int. Tin Res. Inst. reported that the annual world consumption per annum of organotin compounds was 55000 tons in 1988. The physiologically active R_3SnX was about 10000 tons and the other R_2SnX_2 and $RSnX_3$ were about 45000 tons [51–53]. In all consumption of organotin compounds, stabilizers for PVC is about 60% and next one is biocidal agents. These two occupy about 90%. The biocidal agents are wood preservatives, antifouling agents, agrochemicals, pharmaceuticals, disinfectants, rodent repellants, protective agents of masonry and stonework, and slime preventing agents. The others are catalysts, glass applications (as easy handling raw materials for inorganic tin compounds (SnO_2)), water repellents, flame retardants. These uses are shown in Table 10.2 [54]. These uses take advantage of the following two characteristics of organotin compounds. The first is a strong affinity of the tin atom to a donor ligand atom such as sulfur, oxygen and nitrogen. The second one is a physiological characteristic such as biocidal activities (e.g., bactericidal, fungicidal, acaricidal, insecticidal and molluscicidal) and repellent activity against wood-destroying organisms, marine animals, marine plants and rodents.

R_3Sn compounds having biocidal activities are easily decomposed to give nontoxic inorganic tin compounds. This fact is confirmed by many experiments. But the following facts have been gradually evidenced: the great amount of antifouling paints for ships have been used around the world for a long time. A small amount of the paint which is released from the bottom of the ship is able to reach a depth where light does not shine and the decomposition of these organotin compounds becomes very slow. Then organotins may be concentrated in fish and shellfish via planktons in some bays. Organotin compounds were suspected as a cause of the damage to oysters in 1985. The regulation of the uses of organotin compounds started in France, and afterwards similar regulations were also enacted in the United States, Europe and Japan.

Even if the damage to oysters in several bays in Europe and the United States were caused by organotin compounds, organotin compounds should not be considered in the same light as such organometallic compounds as organomercury or organolead. The organotin researchers hope for many people to understand that tin is a safe element based on the following six items [55–61].

(1) Tin is one of important indispensable elements in the human body [56,57].
(2) The tissue of a human or mouse contains a small amount of tin as shown in Table 10.3. The amount is far more than the amount of tin that was recently detected and became an issue in fish and shellfish [58].

Table 10.2 Industrial applications of organotin compounds [54]

Application	Compound
	R_3SnX
Agriculture	
fungicides	$Ph_3SnX (X = OH, OAc)$
antifeedants	$Ph_3SnX (X = OH, OAc)$
acaricides	(c-$C_6H_{11})_3SnX$ (X = OH)  $-N\underset{H}{C}{=}N\underset{H}{C}{=}N)$ $(Ph(CH_3)_2CCH_2)_3Sn)_2O$
Antifouling paint biocides	Ph_3SnX (X = OH, OAc, F, Cl, SCS, $N(CH_3)_2$' $OCOCH_2Cl$, $OCOC_5H_4N$–3), $Ph_3SnOCOCH_2CBr_2COOSnPh_3$, Ph_3SnX (X = F, Cl, OAc), $(Bu_3Sn)_2O$, $Bu_3SnOCOCH_2CBr_2COOSnBu_3$, $(-CH_2C(CH_3)(COOSnBu_3)\text{-})_n$
Wood preservative fungicides	$(Bu_3Sn)_2O$, Bu_3Sn (naphthalenate), $(Bu_3Sn)_3PO_4$
Stone preservation	$(Bu_3Sn)_2O$
Disinfectants	$Bu_3SnOCOPh$, $(Bu_3Sn)_2O$
Molluscicides (field trials)	Bu_3SnF, $(Bu_3Sn)_2O$
	R_2SnX_2
Heat and light stabilizers for rigid PVC	$R_2Sn(SCH_2COO$-i-$Oct)_2$ (R = Me, Bu, Oct, $BuOCOCH_2CH_2$) $(R_2SnOCOCH{=}CHCOO)_n$ (R = Bu, Oct) $Bu_2Sn(OCOCH{=}CHCOOOct)_2$, $Bu_2Sn(OCOC_{11}H_{23})_2$, $Bu_2Sn(SC_{12}H_{25})_2$
Homogeneous catalysts for RTV silicon, polyurethane foams and transesterification reactions	$Bu_2Sn(OCOCH_3)_2$, $Bu_2Sn(OCOC$-i-$Oct)_2$, $Bu_2Sn(OCOC_{12}H_{25})_2$, $Bu_2Sn(OCOC_{11}H_{23})_2$ $(Bu_2SnO)_n$
Precursor for forming SnO_2 films on glass	Me_2SnCl_2
Anthelmintics for poultry	$Bu_2Sn(OCOC_{11}H_{23})_2$
	$RSnX_3$
Heat stabilizers for rigid PVC	$RSn(SCH_2COO$-i-$Oct)_3$ (R = Me, Bu, Oct, $BuOCOCH_2CH_2$) $(BuSnS_{1.5})_4$
Homogeneous catalysts for transesterification reactions	$(BuSn(O)OH)_n$, $BuSn(OH)_2Cl$
Precursor for SnO_2 films on glass	$BuSnCl_3$, $MeSnCl_3$†

†These compounds are used in combination with the corresponding R_2SnX_2 derivatives

Table 10.3 Tin concentration in selected organs of mouse and human [58]

Organ	Sn concentration (ppm)
lung	5.2
stomach	5.4
intestines	6.0
brain	5.5
kidneys	3.5
liver	2.2
thymus	11.6
Tin concentration in human organs	
brain	6.8
gall bladder	2.8
small intestines	2.0
breast tissue	2.4
thymus	12.8

(3) In organotin compounds, the most physiologically active R_3Sn type compounds are the most rapidly decomposed, and they decompose to low physiologically active R_2Sn-type and RSn-type compounds. Finally they become quite nontoxic inorganic tin compounds.

(4) If organotin compounds or inorganic tin compounds are ingested in a living body, the rate of elimination from the system is rapid and they are eliminated almost 100% in a very short period [57]. For example, tributyltin fluoride is dosed for oral administration of 40μg/g (40ppm) in rat. Larger amounts of dibutyltin, monobutyltin and inorganic tin, which are the metabolic products of tributyltin, rather than the intact tributyltin are detected in the liver and kidney even from the first day. It shows that the rate of dealkylation is high. Almost all has disappeared within eight days. The half-life is three or four days [59,60].

(5) Tin is used for tableware and cans. There are no problems if we have ingested tin for a long time from these. It is reported that tin is not accumulated in the body even if we ingest more than 130mg/day [61–61e].

(6) The organotin compounds of R_2Sn type compound exhibit no poisonous characteristics in cells. They are used as anthelmintics for hens and turkeys. Organotin compounds have been investigated for anticancer drugs since they inhibit the growth of tumor cells and they are also used as a remedy for hyperbilirubinemia.

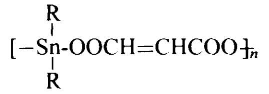
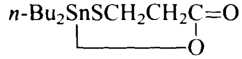
As mentioned above, tin is an entirely different element from toxic heavy metal elements. Moreover please refer to *Organotin Chemistry* or other books for detail on the application of organotin compounds [62–65a].

10.6.1 PVC STABILIZERS

Organotin compounds were first used as stabilizers for polyvinyl chloride (PVC) in 1940 [66]. Since then the uses of organotin compounds have rapidly increased. PVC plastics have the second largest production volume after polyethylene: the total production in the major PVC producing countries was about 12 million tons in 1995 [67]. Thus the amounts of added stabilizer become large. PVC stabilizers are lead compounds, metal soaps and organic compounds, besides organotin compounds. Organotin compounds are a very efficient heat stabilizer in only small amounts, a high degree of clarity is obtained when using it as an addition for transparent PVC, and they have a low mammalian toxicity compared to other stabilizers. In particular, they are suitable for food-contacting applications [68]. Some representative PVC stabilizers are shown in Table 10.4. The low molecular weight model compounds for PVC are stable up to 300–330 °C. But commercial PVC is starting to decompose at 90–130 °C. Hence, PVC requires stabilizers for thermal degradation during formation as well as stabilizers for photodegradation for outdoor uses. The organotin compounds shown in Table 10.4 are able to protect the thermal decomposition of PVC effectively with only 1 g or less to 100 g of resin. Many stabilization mechanisms of organotin PVC stabilizers have been reported since the 1950s. In these reports, the most important reports are the three articles published by Frye *et al.* in 1964 [69–71]. They studied the PVC stabilization mechanism of organotin compounds by a radioactive tracer technique with the labels (^{14}C or ^{113}Sn) being located in the R, Sn and Y of R_2SnY_2. They found that organotin compounds retard the zipper reaction of the PVC resin because the Y component of organotin compounds are substituted to liable chlorine atoms of PVC resin.

PVC resin is more decomposable than the model compounds. That is because PVC is formed at many active centers by side reactions in the polymerization of

Table 10.4 Common organotin PVC stabilizers [62,63,65]

Stabilizers		R
Dialkyltin diisooctylthioglycolate $R_2Sn(SCH_2COO\text{-}i\text{-}Oct)_2$		Me, *n*-Bu, *n*-Oct
Dialkyltin maleate	 $[-\underset{\underset{R}{\mid}}{\overset{\overset{R}{\mid}}{Sn}}\text{-OOCH=CHCOO}]_n$	Me, *n*-Bu, *n*-Oct
Dialkyltin maleate ester	$R_2Sn(OOCCH{=}CHCOOR')_2$	Bu, Oct†
Dialkyltin dilaurate	$R_2Sn(OOCC_{11}H_{23})_2$	*n*-Bu, *n*-Oct
Dibutyltin \-mercaptopropionate	 $n\text{-}Bu_2SnSCH_2CH_2\underset{\underset{O}{\mid}}{C}{=}O$	
Diestertin diisooctylthioglycolate	$(n\text{-}BuOOCCH_2CH_2)_2Sn(SCH_2COO\text{-}i\text{-}Oct)_2$	

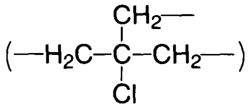
† R′ = Me, *n*-Bu, *i*-Oct.

vinyl chloride as shown in Scheme 10.1 [65]. Evans and Karpel [62] of Int. Tin Res. Inst. reported that the active centers of polyvinyl resins are the following four. The value is the number of active centers per 1000 vinyl monomers [65].

(1) Chain end group	—
(2) Intra-chain branches	0.5–5.4
(3) Unsaturated group	0.1–0.5
(4) Oxidized structures	6–8

The first (chain end groups), are formed by the disproportionation of termination in the PVC polymerization process in Scheme 10.1. The second (intra-chain branches) are produced by a chain transfer as shown in Scheme 10.1, and the third (unsaturated groups ($-CH_2CH{=}CH-CHCl-$)) are formed by the elimination of a chlorine radical (or hydrogen radical) in a chain formed by chain transfer as in Scheme 10.1. The fourth is oxidized structures, the adjacent carbon of intramolecular unsaturated group, that is, allyl carbon is oxidized by the oxygen in air and forms the carbonyl group. The first chain end group of the four active centers is of relatively low reactivity. The decomposition of polyvinyl chloride is considered to occur mainly by the second to fourth active centers. The amount of active centers is different with polymerization conditions of each resin. The decomposition of polyvinylchloride is mainly dehydrochlorination, but under an inert atmosphere, the decomposition rate is proportional to the sum of the second and the third active centers (Figure 10.2 [72–74]). Then, the reactivities of these two active centers are thought to be almost the same.

The chlorine atom at the intra-chain branches

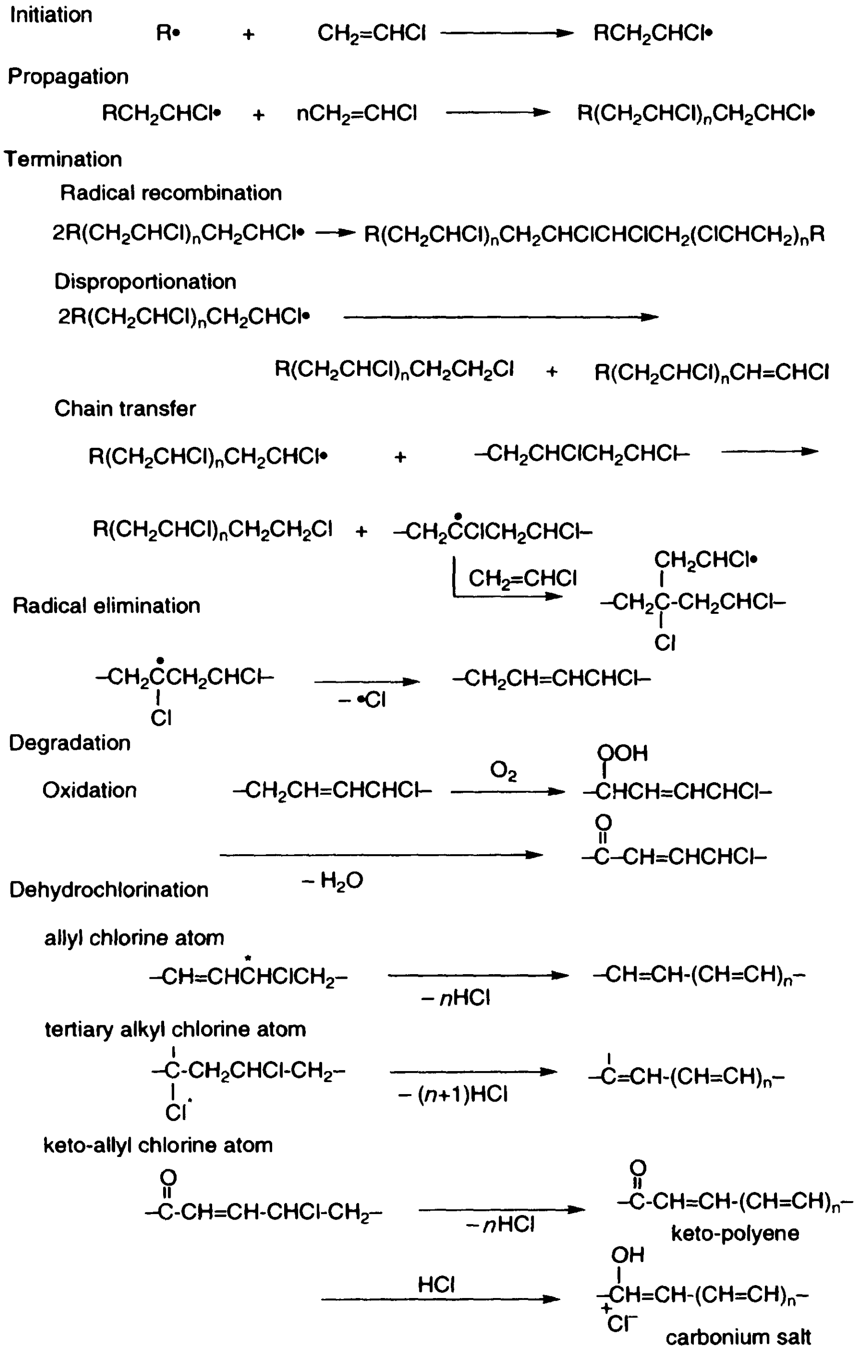


$$(-H_2C-\overset{\displaystyle CH_2-}{\underset{\displaystyle Cl}{C}}-CH_2-)$$

or the chlorine at the allyl position of the unsaturated group react with the adjacent hydrogen, and these dehydrochlorination reactions form the unsaturated bonds and then the formed chlorine atom at the allyl position further reacts with the adjacent hydrogen atom. The decomposition of polyvinyl chlorine resin is caused by such a zipper reaction.

PVC stabilizers (R_2SnY_2) react with active chlorine atoms. They remove the active chlorine atoms so that dehydrochlorination reaction does not proceed. PVC stabilizers work by substituting the active chlorine atom of polyvinyl chloride by the Y group of the PVC stabilizers. This reaction is from A to B shown in Scheme 10.2. XZ in Scheme 10.2 corresponds to Y. Hence, the polymer bonds to the donor atom X of Y when organotin compounds bond to active chlorine atoms, and the polymer is stabilized by organotin compounds.

As mentioned above, Frye and his co-workers confirmed the PVC stabilization mechanism of organotin compounds with a radioactive tracer technique, showing that organotin compounds (R_2SnY_2) act upon PVC by displacement of the active chlorine by the Y group via coordination intermediates of tin compounds. Poller



Initiation

$$R\bullet + CH_2{=}CHCl \longrightarrow RCH_2CHCl\bullet$$

Propagation

$$RCH_2CHCl\bullet + nCH_2{=}CHCl \longrightarrow R(CH_2CHCl)_nCH_2CHCl\bullet$$

Termination

Radical recombination

$$2R(CH_2CHCl)_nCH_2CHCl\bullet \longrightarrow R(CH_2CHCl)_nCH_2CHClCHClCH_2(ClCHCH_2)_nR$$

Disproportionation

$$2R(CH_2CHCl)_nCH_2CHCl\bullet \longrightarrow R(CH_2CHCl)_nCH_2CH_2Cl + R(CH_2CHCl)_nCH{=}CHCl$$

Chain transfer

$$R(CH_2CHCl)_nCH_2CHCl\bullet + -CH_2CHClCH_2CHCl- \longrightarrow R(CH_2CHCl)_nCH_2CH_2Cl + -CH_2\dot{C}ClCH_2CHCl-$$

$$-CH_2\dot{C}ClCH_2CHCl- \xrightarrow{CH_2{=}CHCl} -CH_2\underset{Cl}{\overset{CH_2CHCl\bullet}{C}}-CH_2CHCl-$$

Radical elimination

$$-CH_2\underset{Cl}{\dot{C}}CH_2CHCl- \xrightarrow[-\bullet Cl]{} -CH_2CH{=}CHCHCl-$$

Degradation

Oxidation

$$-CH_2CH{=}CHCHCl- \xrightarrow{O_2} -\overset{OOH}{C}HCH{=}CHCHCl- \xrightarrow[-H_2O]{} -\overset{O}{\overset{\|}{C}}-CH{=}CHCHCl-$$

Dehydrochlorination

allyl chlorine atom

$$-CH{=}CH\overset{*}{C}HClCH_2- \xrightarrow[-nHCl]{} -CH{=}CH-(CH{=}CH)_n-$$

tertiary alkyl chlorine atom

$$-\underset{Cl^{*}}{\overset{|}{C}}-CH_2CHCl-CH_2- \xrightarrow[-(n+1)HCl]{} -\overset{|}{C}{=}CH-(CH{=}CH)_n-$$

keto-allyl chlorine atom

$$-\overset{O}{\overset{\|}{C}}-CH{=}CH-CHCl-CH_2- \xrightarrow[-nHCl]{} -\overset{O}{\overset{\|}{C}}-CH{=}CH-(CH{=}CH)_n-$$

keto-polyene

$$\xrightarrow{HCl} -\overset{OH}{\underset{+}{C}}H{=}CH-(CH{=}CH)_n- \quad Cl^-$$

carbonium salt

Scheme 10.1 PVC formation and thermal degradation process [65]

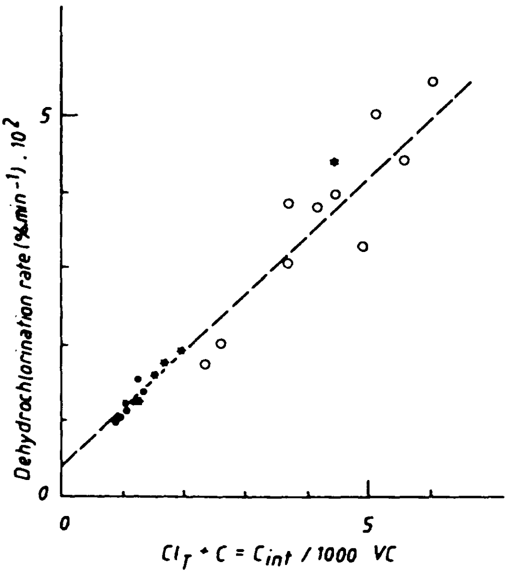
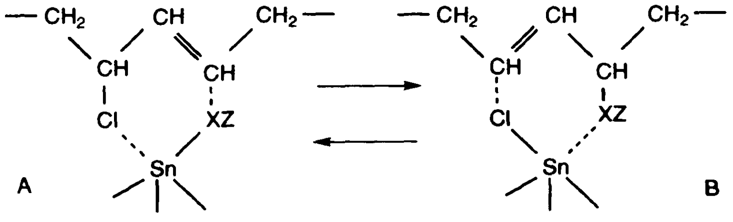


Figure 10.2 Dehydrochlorination rate versus tertiary chlorine atoms + internal double bonds [72]: ● fractionated commercial suspension PVC, polymerization temperature 55 °C [73,74], ○PVC polymerized at reduced monomer pressure, polymerization temperature 55 °C, monomer pressure between 59–92% of the saturation pressure of vinyl chloride at 55 °C [73,74], *bulk and suspension polymerization by IUPAC Sub-Group on Defects in the Molecular Structure of PVC and their relation to thermal stability. [Modified from [72].]



X = donor atom

XZ = corresponding to the Y in the previous formula (R_2SnY_2) as PVC stabilizers

Scheme 10.2

also confirms the displacement reaction of the active chlorine by the Y group with 3-chlorobut-1-ene as a model compound, and further with a radioactive tracer technique using $Bu_2Sn(^{35}SBu)_2$ as a PVC stabilizer [75–77]. On the basis of Scheme 10.2 (Fryrs's mechanism), organotin PVC stabilizers require the following three conditions:

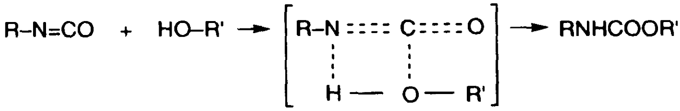
(1) The tin atom has at least one donor atom such as oxygen or sulfur (see Table 10.4). The donor atom is X in Scheme 10.2.

(2) The tin atom has at least one coordination site to bond with an active chlorine atom, that is, the coordination of tin is five or less.

(3) The donor atom has a reasonable reactivity with a PVC polymer chain at 180–200 °C, plastic molding temperatures of polyvinyl resins, but the bond of the donor atom with tin also has a reasonable stability as a PVC stabilizer during the processing. If PVC stabilizers begin to decompose at lower temperatures than the decomposition temperatures (90–130 °C) of the commercial PVC and the disappearance rate of PVC stabilizer is high, then we cannot expect the effect to last.

10.6.2 CATALYSTS

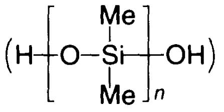
The applications of the strong affinity to oxygen of organotin compounds are as catalysts. Organotin compounds are used for the polymerization of polyurethanes, polymerization of silicones and esterifications as the catalysts [62,63,65]. The catalysts for reactions of phenylisocyanate with butanol as a basic reaction of polyurethane formation reaction are shown in Table 10.5 [78]. The reaction rate with dialkyltin compounds are 30000–80000 times faster compared with the reaction without a catalyst. The urethane is considered to be formed via the following four center mechanism [79].



$$R\text{-}N{=}CO + HO\text{-}R' \rightarrow \left[\begin{array}{ccc} R\text{-}N & \cdots & C\cdots O \\ \vdots & & \vdots \\ H & — & O — R' \end{array}\right] \rightarrow RNHCOOR' \qquad (10.24)$$

But, recently, van der Weij [79a,79b] and Odera and Ohkkawara [79c] proposed that alkoxytin is formed by coordination of alkoxy oxygen at the first step, isocyanate reacts with it to form urethane bond and further the alcohol reacts with it to form alkoxytin and urethane.

In silicones, organotin compounds are used for the formulation of RTV silicone elastomers. These are reactions of silicones



$$\left(H\!\left[O\text{-}\overset{Me}{\underset{Me}{Si}}\right]_n\!OH\right)$$

with a vulcanization agent, $Si(OEt)_4$, in the presence of $R_2Sn(OOCR')_2$ as the catalyst. The actual catalyst is thought to be the hydrolysis product ($R_2Sn(OOCR')OH$), in which one oxycarbonyl group (OOCR) is substituted with

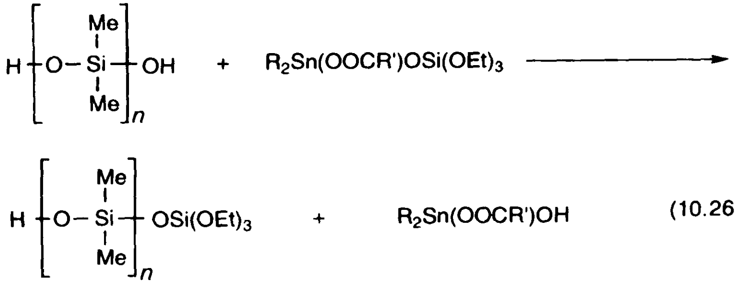
Table 10.5 Comparison of catalytic efficiency of some organotins and amines of the phenyl isocyanate–butanol reaction [78]

Catalyst	Relative activity at 1.0 mol%
none	1
N-methylmorpholine	4
triethylamine	8
N,*N*,*N*′, *N*′-tetramethyl-1,3-butanediamine	27
1,4-diazabicyclo[2.2.2]octane	120
tetra-*n*-butyltin	160
tin(II) chloride	2200
tin(IV) chloride	2600
tri-*n*-butyltin acetate	31 000
di-*n*-butyltin diacetate	56 000
di-*n*-butyltin dilaurate	56 000
di-*n*-butyltin dichloride	57 000
di-*n*-butyltin dilaurylmercaptide	71 000
dimethyltin dichloride	78 000

OH, since no vulcanization occurs under anhydrous conditions. The active hydrolysis product reacts with ethoxy silane group of the crosslink agent to form an organotin silanoate (10.25).

$$R_2Sn(OOCR')OH + Si(OEt)_4 \longrightarrow R_2Sn(OOCR')OSi(OEt)_3 + EtOH \qquad (10.25)$$

The silanoate then reacts with polydimethylsiloxane to give an ethoxy-substituted silicone polymer to regenerate the catalyst. The catalysts react the crosslinking agent again. Thus, the crosslinking reaction proceeds [80].



$$H\left[O-\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}\right]_n OH + R_2Sn(OOCR')OSi(OEt)_3 \longrightarrow H\left[O-\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}\right]_n OSi(OEt)_3 + R_2Sn(OOCR')OH \qquad (10.26)$$

The esterifications traditionally employ strong acid catalysts such as *p*-toluenesulfonic acid. Recently it has been found that organotin compounds are also good catalysts. They have the following advantages over the traditional catalysts: (i) a pure product is obtained since side-reactions are greatly reduced, (ii) acid-induced corrosion of the process equipment is virtually eliminated, (iii) they are highly efficient and need only be incorporated at levels of about 0.05 to 0.30%.

Table 10.6 Comparison of catalysts for adipic acid/2-ethylhexanol; fusion method, nitrogen atmosphere, reaction time 4 hours [81]

Catalyst (0.15% w/w)	Temperature range (°C)	Final acid no.
none	200–220	23.7
p-toluenesulphonic acid	128–170	18.9
tetrabutyl titanate	180–220	2.8
dibutyltin diacetate	170–220	0.4

An illustration of the high catalytic activity is shown in Table 10.6 [81].

Organotin compounds are used as polymerization catalysts for olefin. In the alkylaluminum and $TiCl_4$ of Ziegler–Natta catalysts, if organotin compounds are used in place of liable aluminum compounds, they are more easily handled. For example, in a low pressure polymerization of ethylene, with Ph_4Sn, $AlCl_3$ and a small amount of VCl_4 as the catalysts, the reaction gives polymers having a linear and narrow molecular weight distribution [82].

10.6.3 WOOD PRESERVATIVES

Van der Kerk of Holland [83–85] first reported that organotin compounds are effective wood preservatives in 1954. The relative fungicidal activities of organotin compounds are shown in Table 10.7 [83].

The order of reactivity is as follows:

$$R_3SnX > R_4Sn \approx R_2SnX_2 > RSnCl_3$$

Table 10.7 Fungicidal properties of organotin compounds [83]

Compound	Concentration (ppm. = mg/l) causing complete inhibition of growth of the fungi: Botrytis allii	Penicillium italicum	Aspergillus niger	Rhizopus nigricans
Et_4Sn	50	> 1000	100	100
Et_3SnCl	0.5	2	5	2
Et_2SnCl_2	100	100	500	200
$EtSnCl_3$	> 1000	> 1000	> 1000	> 1000
$Me_3SnOOCMe$	20	20	200	200
$Et_3SnOOCMe$	1	2	5	2
$Pr_3SnOOCMe$	0.1	0.1	1	1
$Bu_3SnOOCMe$	< 0.1	< 0.1	0.5	0.5
$(C_6H_{13})_3SnOOCMe$	1	10	20	100
$Oct_3SnOOCMe$	> 100	> 100	> 100	> 100
$Ph_3SnOOCMe$	2	1	0.5	10
Et_4Sn	50	> 1000	100	100

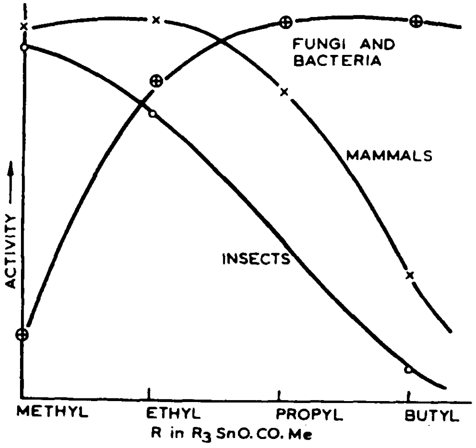


Figure 10.3 Dependence of the biological activity of tri-*n*-alkyltin acetates on the nature of the alkyl gruop for different species [86].

Hence, R_3SnX is the most effective. Van der Kerk found that tributyltin has the optimal fungicidal activity. They found that the X group in R_3SnX did not substantially influence their fungitoxicity; however, the R group has a great effect on the activity. These trialkyltin compounds have been shown in mammals to be strong inhibitors of oxidative phosphorylation in mitochondria. The biological activities of trialkyltin compounds are shown in Figure 10.3 [86] and Table 10.8 [87,88]. Tributyltin is widely used since it possesses a tolerable mammalian toxicity whilst it has a high toxicity to fungi and gram-positive bacteria. In particular, tributyltin oxide (TBTO) is used as a wood preservative. It is thought that Bu_3Sn reacts with the hydroxyl group of cellulose of woods and trialkyltin are stably sustained on the surface of woods [52].

Tributyltin oxide (TBTO) is required in amounts of about 0.2 kg per cubic meter of wood: the weight ratio of TBTO and wood is 1 : 1300. Cellulose is constituted per 5000 glucose units. The above ratio is corresponding to TBTO and cellulose

Table 10.8 Dependence of the biological activity of triorganotin compounds on the nature of the organic group for various species [87,88]

Species	R in most active R_3SnX compounds
insects	Me
mammals	Et
gram-negative bacteria	Pr
gram-positive bacteria, fish, fungi and molluscs	Bu
fish, fungi, molluscs and mites	Cy, $PhC(Me)_2CH_2$

unit. That is, TBTO bonds to the end of long cellulose chain and protects the cellulose from attack by fungi [89]. When TBTO is used as a wood preservative, it disproportionates dibutyltin and tetrabutyltin (bp 127°C/1.7mmHg) via Bu_3SnOX,

$$(Bu_3Sn)_2O \longrightarrow Bu_3SnOX \longrightarrow Bu_2Sn(OX)_2 + Bu_4Sn \quad (10.27)$$

and the tetrabutyltin gradually evaporated. For example, at 25°C, TBTO decreases by 25% in 14 weeks, and dibutyltin formed is 10% [90]. However, the effect is still retained after 25 years since the wood preservative started to be used. Hence, the effect of wood preservatives is retained during their decomposition process. Recently, the polymeric derivatives of butyltin with a copolymer of metacrylate and maleic acid anhydride has been developed and they are found to have good durability as wood preservatives against biodegradation [91,92].

10.6.4 ANTIFOULANTS

Marine fouling can be a serious problem in the shipping industry, since it increases the surface roughness of the hull and hence its frictional resistance to movement through water. In 1983, Byrne published the following equation between the surface roughness (K, (μ)) and the change of horsepower (P):

$$P = 3.8((K_2)^{1/3} - (K_1)^{1/3})$$

K_1 = initial hull roughness; K_2 = final hull roughness; P = ship performance.

When the surface roughness increases by 30μ, the fuel consumption necessary for maintaining the same speed increases by 1%. Hence, when the surface roughness increases by 1 mm, the fuel consumption increases by 30%. Marine animals and plants such as barnacles and algae adhere to the ships' hull and it can be a serious problem. On account of these reasons, a large amount of organotin compounds have been used in antifouling paint. But environmental problems occurred as described above, and this book will not describe them in further detail [93–97].

10.6.5 AGRICULTURAL CHEMICALS

Triorganotin compounds have a pesticidal activity towards pests of agricultural and horticultural crops. The principal advantage of organotin agrochemicals are the following four points: (i) relatively low phytotoxicity, (ii) low toxicity to non-target organisms, (iii) lack of resistance to them by crop pests, (iv) they undergo degradation in the environment, eventually forming harmless inorganic tin residues.

Trialkyltin compounds are extremely powerful biocides; however, their toxicity to plants is too high for practical uses in agriculture. But triphenyltins showed a sufficiently wide margin between fungitoxicity and phytotoxicity to enable them to be used safely. Triphenyltin compounds have very good adhesive properties and are retained firmly by leaves on which they have been sprayed, even after heavy rainfall.

The representative commercial organotin compounds are triphenyltin acetate, triphenyltin hydroxide, tricyclohexyltin hydroxide, triphenyltin chloride, 1-tricyclohexylstannyl-1,2,4-triazole, bis[tri(2-methyl-2-phenylpropyl)tin] oxide, bis(trineophyltin) oxide, etc. [98–100]. For example, triphenyltin acetate has a broad spectrum of activity against a number of fungal diseases, such as early blight, down mildew, anthracnose, leaf and pod spot, among others, and can be used on a variety of crops, such as beans, celery, carrots, cocoa, coffee, hops, onions, potatoes, rice, sugar beets, etc. It also exhibits algicidal and molluscicidal properties, and is effective for use in rice paddy fields and against water snails in fish ponds. Triphenyl hydroxide is also used as a fungicide, particularly against tuber blight in potatoes, where it eradicates blight and protects the foliage from further infection. It is also used to control leaf spot in sugar beet, and has strong bactericidal properties. Triphenyltin chloride is also a fungicide and acts as a rodent repellent [100]. Tricyclohexyl compounds are good miticides. They are the acetate, hydroxide and halide. An environmental impact test of radio-labeled tricyclohexyltin hydroxide has been carried out in rats. The test shows that 99.9% of the labeled compound was excreted, indicating no significant absorption in the gastrointestinal tracts. The metabolism of the compound in animals occurs by the stepwise cleavage of cyclohexyl groups from the tin atom [101].

10.6.6 PHARMACEUTICALS

Organotin compounds have also been developed as pharmaceuticals such as anthelmintics, disinfectants and antitumor drugs [102–116]. Dialkytin compounds are applied as anthelmintics. For example, dibutyltin dilaurate is used for tapeworm in chickens or turkeys, and coccidiosis and hexamitiasis in turkeys, while dibutyltin oxide is used for intestinal worms in fresh water fish such as trout.

As shown in Table 10.7, tributyltin compounds are active against gram-positive bacteria. Their combination with a second chemical which combats gram-negative bacteria produces a highly effective disinfectant which may be used on open areas posing a risk of infection, such as hospital floors and sports pavilions. Common formulations contain, for example, a mixture of tributyltin benzoate and formaldehyde, or tributyltin oxide and a quaternary ammonium halide [4].

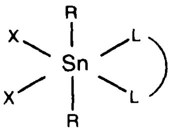
$R_2SnX_2L_2$ ($R = Me$, Et, *n*-Pr, *n*-Bu, Ph; $X = Cl$, Br, I, SCN; $L =$ oxygen or nitrogen donor ligand) are synthesized for antitumor drugs by taking cisplatin (*cis*-$Pt(NH_3)_2Cl_2$) as a model compound. Many investigations of antitumor drugs with organotin compounds are carried out on four-coordination and six-coordination, the others are five-coordination. Bulten and co-workers [108] have widely investigated on the antitumor activity of four-coordination organotin compounds. The results are shown in Table 10.9. In these compounds, the compounds having Sn–O bond or the compounds which form Sn–O bond by the hydrolysis, have high activity. For example, if $RR'Sn(CH_2COOMe)_2$ and $RR'Sn(CH_2CH_2COOMe)_2$ are compared, the former ($RR'Sn(CH_2COOMe)_2$) is easily hydrolyzed to give a Sn–O bond. Therefore the former is active but the latter is stable to hydrolysis and it is inactive.

Table 10.9 Antitumor screening data of a number of organotin compounds against P388 lymphocytic leukemia in mice [108]

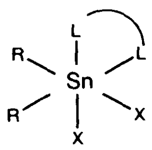
Compound	Optimum dose (mg/kg)	Maximum T/C^{+}
$(RR'ClSn)_2O$		
R,R' = Me,Me	12.5	125–141
Et, Et	8	120
Bu,Bu	—	inactive
Et,Bu	6.25	137
Ph,Ph	1.56	137
o-Tol, *o*-Tol	1.56	125–133
p-Tol, *p*-Tol	12.5	141
p-Cl-Ph, *p*-Cl-Ph	12.5	146
$Ph_2SnClOH$	25	132–198
	12.5	144–163
RR'SnO		
RR' = Et,Et	25	154
Ph,Ph	4	133
Et,Ph	50	125–147
Bu,Ph	100	116
$RR'Sn(CH_2COOMe)_2$		
RR' = Me,Me	16	128
Et,Et	12.5	170
Ph,Ph	5	133
Et,Ph	50	143–181
$RR'Sn(CH_2CH_2COOMe)_2$	—	inactive

$^{+}$T/C is the ratio of the survival time (in days) of treated (T) and untreated (C) mice. A compound is considered to be active at T/C values > 120%.

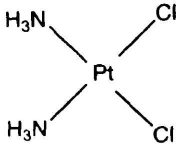
Halogen or nitrogen atoms of cisplatin are in the cis position. But, organotin compounds are not formed in planar four coordination as the cisplatin. However, the octahedral structure of six-coordination is able to form partly cis structure on halogen or nitrogen atoms similar to cisplatin.



I

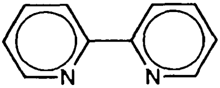


II



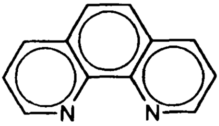
cisplatin

As organotin compounds with primary or secondary amine (L) are liable, the following divalent amines are used as L. Although the T/C% (median survival time of the treated mice group divided by that of the control group towards P388 lymphocytic leukemia, per cent) obtained for the organotin compounds were lower (120–180%) than those found for the platinum derivatives (200–300%) against the same tumor system, there is no evidence to suggest that organotin compounds display a high nephrotoxicity, as do many of the platinum complexes [63,105]. In particular, ethyl and phenyl organotin compounds show high antitumor activities as shown in Table 10.10 [105].



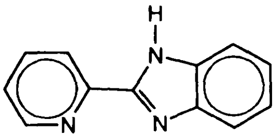
bipy

2,2-bipyridyl



phen

1,10-phenanthroline



PBI

2-(2-pyridyl)benzimidazole

It is thought that the two chlorine atoms in cisplatin are dissociated in the organism and Pt forms a coordination bond with two N-7 atoms of the adjacent guanidine of DNA.

In a recent study of metallocene dichloride $(Cp)_2MCl_2$ (M = Ti, V, Nb, Mo), only those compounds for which the Cl–M–Cl angle is < 95°, giving a bite size of

Table 10.10 The activity of $R_2SnX_2{\cdot}L_2$ towards P388 lymphocytic leukemia [105]

Compound ($R_2SnX_2{\cdot}L_2$)			Two best test results	
R	X	L or L_2	(T/C%) (Dose mg/kg)	
Me	Cl	py	125/25	121/50
		bipy	126/50	120/50
	Br	bipy†	135/200	131/100
Et	F	phen†	138/6.25	133/12.50
	Cl	phen†	177/50	176/100
		PBI†	171/100	171/100
	Br	PBI†	175/12.50	161/25
		phen†	176/25	166/50
	I	phen†	184/200	166/100
	NCS	phen†	164/100	149/100
		bipy†	179/12.50	166/25
Pr	Cl	phen†	127/100	125/50
	Br	phen†	140/50	121/25
Bu	Cl	phen†	141/100	126/200
Ph	Cl	PBI†	164/100	141/50
	Br	TMphen†	177/6.25	156/6.25
Oct	Cl	phen	inactive	

†Selected for further tests. TMphen = 3,4,7,8-tetramethyl-1,10-phenanthroline

Table 10.11 Crystallographic and antitumor activity (P388 lymphocytic leukaemia) data for diorganotin dihalides [113]

Compound	ClSnCl (°)	Cl–Cl (Å)	Average Sn–N (Å)	Best T/C %[a]	
Ph_2SnCl_2·bipy	103.5	3.94	2.36	103	inactive
Et_2SnCl_2·bipy	104.2	4.00	2.38	115	inactive
Bu_2SnCl_2·phen[b]	105	4.05	2.39	141	active
Bu_2SnCl_2·bipy	104.3	4.00	2.40	131	active
Et_2SnCl_2·phen	105.2	4.02	2.41	176	active
Et_2SnCl_2·pdt[c]	103.2	3.88	2.50	144	active

[a] Median survival time of treated group of mice divided by that of the control group a compound is active if it has a T/C > 120%.

[b] 1,10-phenanthroline.

[c] 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine.

< 3.6 Å (the upper limit for DNA–metal crosslinks), are active [105]. The latter 3.6 Å is thought to be the best value which DNA forms the bridge bond with metal atom [103].

As to the X-ray structure parameters of six diorganotin dihalide complexes, $R_2SnX_2 \cdot L_2$ have also been examined as shown in Table 10.11 [113]. It was found that the Cl–M–Cl bond angles of both active and inactive compounds are all of a similar magnitude (ca. 103–105°) and well above the limiting value (> 95°). Hence it is thought that the mode of action for the formation of a metal–base cross-link of the organotin takes place via a different route [113]. For the other type of organotin compound, e.g., $Ph_2SnClOH$, the T/C% also shows a higher data, 198% [108,109].

The relation of the structure of organotin compounds and their activity is not found from the data of X-ray diffraction and Mössbauer spectroscopy (Table 10.11) [105,106]. The organotin compounds are considered to act in an entirely different way from cisplatin.

The other five-coordination compounds such as glycylglycinates have been investigated [103,104,111,114,116].

The compounds having not only nitrogen but also oxygen or sulfur as coordination atoms also show antitumor activity [103]. The activity (T/C) of organotin compounds is about 200% lower than those of the platinum derivatives (200–300%) against the same tumor system, as organotin compounds do not show nephrotoxicities. Sn is expected to show lower side effects.

The other drugs of organotin compounds are investigated for the preventative drugs of hyperbilirubinemia [103].

10.6.7 MISCELLANEOUS USES

The miscellaneous uses of organotin compounds include textile treatments, glass surface treatment, protecting masonry and stonework, and slime prevention, water repellent, etc. [51]. Bis(tributyltin) oxide is also useful for the prevention of fungal attack on cellulose material such as cotton textile and in cellulose-based household fillers as wood preservatives described above [4].

Monoorganotin trichloride, diorganotin chloride or their mixtures, e.g., monobutyltin trichloride and dimethyltin dichloride, are used as precursors for forming surface films of SnO_2 at high temperatures. They are vaporized and brought into contact with the glass surface in the presence of air, at about 600°C, whereupon decomposition and oxidation to tin (IV) oxide occurs at the glass surface [62,63]. The fact that thin films of tin (IV) oxide less than 100nm thickness would increase the strength and impact resistance of glassware was known [63]. This compound has a low vapor pressure, and is less susceptible to hydrolysis and fuming, which leads to its easier handling than the alternative coating precursor, tin (IV) chloride [117].

Treatments based on monoorganotin compounds such as $(Me_4N)^+{}_2(BuSnCl_5)^{2-}$ conferred an adequate flame resistance to wool gabardine fabrics [62]. Trialkyltin or triaryltin compounds such as bis(tributyltin) oxide and triphenyltin chloride have a biocidal effect against clothes-moth and carpet-beetle [62,63]. These organotin compounds also have biocidal activities against moss, algae, and lichens on stonework, slime-forming bacteria, fungi and algae in the paper industry, etc. [62,63].

The other uses of organotin compounds are as the antiabrasion improvers of lubricant of alkylphenyltin compounds $(R_nSn(OC_6H_4\text{-}C_{10}H_{21})_{4-n}$, $R = Et$, Bu, $n = 2,3)$ [118].

REFERENCES

[1] I. Omae, *Organotin Chemistry*, *J. Organometallic Chemistry Library 21*, Elsevier, Amsterdam, 1989.

[2] R.C. Poller, *The Chemistry of Organotin Compounds*, Logos, London, 1970.

[3] P.G. Harrison, *Chemistry of Tin*, Blackie, London, 1989.

[4] A.G. Davies and P.J. Smith, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.2, p.519, 1982.

[5] R.K. Ingham, S.D. Rosenberg and H. Gilman, *Chem. Rev.*, **60** (1960) 459.

[6] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.

[7] *Kogyo Binran*, Tsusyo Sangyo Chosakai Shuppanbu, 1997.

[8] S. Matsuda and H. Matsuda, *Kogyo Kagaku Zasshi*, **63** (1960) 114.

[9] H. Matsuda and S. Matsuda, *Kogyo Kagaku Zasshi*, **63** (1960) 1958.

[10] H. Matsuda and S. Matsuda, *Kogyo Kagaku Zasshi*, **63** (1960) 1965.

[11] H. Matsuda, H. Taniguchi and S. Matsuda, *Kogyo Kagaku Zasshi*, **64** (1961) 541.

[12] S. Matsuda and H. Matsuda, *Bull. Chem. Soc. Japan*, **35** (1962) 208.

[13] H. Matsuda, J. Hayashi and S. Matsuda, *Kogyo Kagaku Zasshi*, **64** (1961) 1951.

[14] H. Matsuda, M. Nakamura and S. Matsuda, *Kogyo Kagaku Zasshi*, **64** (1961) 1948.

[15] S. Kikkawa and S. Matsuda, *Kogyo Kagaku Zasshi*, **67** (1964) 852.

[16] S. Matsuda, S. Kikkawa and I. Omae, *Kagyo Kagaku Zasshi*, **69** (1966) 646.

[17] I. Omae, S. Matsuda, S. Kikkawa and R. Sato, *Kogyo Kagaku Zasshi*, **70** (1967) 705.

[18] I. Omae, S. Onishi and S. Matsuda, *Kogyo Kagaku Zasshi*, **70** (1967) 1755.

[19] I. Omae, S. Matsuda and S. Kikkawa, *Kogyo Kagaku Zasshi*, **70** (1967) 1759.

[20] M. Yoshida, T. Ueki, N. Yasuoka, N. Kasai, M. Kakudo, I. Omae, S. Kikkawa and S. Matsuda, *Bull. Chem. Soc. Japan*, **41** (1968) 1113.

[20a] S. Matsuda, S. Kikkawa and I. Omae, *J. Organomet. Chem.*, **18** (1969) 95.

[21] I. Omae, S. Onishi and S. Matsuda, *J. Organomet. Chem.*, **22** (1970) 623.

[22] I. Omae, K. Yamaguchi and S. Kikkawa, *J. Organomet. Chem.*, **24** (1970) 663.

[23] T. Kimura, T. Ueki, N. Yasuoka, N. Kasai, N. Kakudo, I. Omae, S. Kikkawa and S. Matsuda, *21st Annual Meeting of the Chemical Society of Japan, Osaka, 1968*, vol. 1, p.176; T. Kimura, T. Ueki, N. Yasuoka, N. Kasai and M. Kakudo, *Bull. Chem. Soc. Japan*, **42** (1969) 2479.

[24] I. Omae, *Rev. Silicon, Germanium, Tin and Lead Compounds*, **1** (1972) 59.

[25] I. Omae, *Kagaku no Ryoiki*, **33** (1979) 767.

[26] I. Omae, *Kagaku Kogyo*, **33** (1982) 989.

[27] S. Matsuda, S. Kikkawa and M. Nomura, *Kogyo Kagaku Zasshi*, **69** (1966) 649.

[28] M. Nomura, S. Matsuda and S. Kikkawa, *Kogyo Kagaku Zasshi*, **70** (1967) 710.

[29] M. Nomura, S. Ando and S. Kikkawa, *Kogyo Kagaku Zasshi*, **71** (1968) 394.

[30] M. Nomura, N. Kashiwagi, S. Kikkawa and S. Matsuda, *Kogyo Kagaku Zasshi*, **71** (1968) 1021.

[31] M. Nomura, N. Matsui and S. Matsuda, *Kogyo Kagaku Zasshi*, **71** (1968) 1526.

[32] M. Nomura, N. Matsui and S. Matsuda, *Kogyo Kagaku Zasshi*, **72** (1969) 1206.

[33] S. Matsuda and M. Nomura, *J. Organomet. Chem.*, **25** (1970) 101.

[34] S. Matsuda, S. Kikkawa and N. Kashiwa, *Kogyo Kagaku Zasshi*, **69** (1966) 1036.

[34a] S. Matsuda, S. Kikkawa and T. Hayashi, *Kogyo Kagaku Zasshi*, **69** (1966) 256.

[34b] S. Matsuda, S. Kikkawa and T. Hayashi, *Technol. Rep. Osaka, Univ.*, vol. 17, No. 766, p. 193 (1967).

[34c] T. Hayashi, S. Kikkawa and S. Matsuda, *Kogyo Kagaku Zasshi*, **71** (1968) 710.

[44d] T. Hayashi, J. Uchimura, S. Matsuda and S. Kikkawa, *Kogyo Kagaku Zasshi*, **70** (1967) 714.

[34e] T. Hayashi, S. Kikkawa and S. Matsuda, *Kogyo Kagaku Zasshi*, **70** (1967) 1389.

[34f] T. Hayashi, S. Kikkawa, J. Uchimura and S. Matsuda, *Tech. Rep. Osaka, Univ.*, vol. 18, No. 821, p. 233 (1968).

[34g] T. Hayashi, S. Kikkawa, S. Matsuda and K. Fujita, *Kogyo Kagaku Zasshi*, **70** (1967) 2298.

[35] J. Boivin, J. Camara and S.Z. Zard, *J. Am. Chem. Soc.*, **114** (1992) 7909.

[36] I. Ryu, H. Yamazaki, K. Kusano, A. Ogawa and N. Sonoda, *J. Am. Chem. Soc.*, **113** (1991) 8558.

[37] P.J. Davidson and M. F Lappert, *J Chem. Soc. Chem. Commun.*, (1973) 317.

[38] D.E. Goldberg, D.H. Harris, M.F. Lappert and K.M. Thomas, *J. Chem. Soc. Chem. Commun.* (1976) 261.

[39] M. Kira, R. Yauchibara, R. Hirano, C. Kabuto and H. Sakurai, *J. Am. Chem. Soc.*, **113** (1991) 7785.

[40] B.S. Jolly, M.F. Lappert, L.M. Engelhardt, A.H. White and C.L. Raston, *J. Chem. Soc. Dalton Trans.*, (1993) 2653.

[40a] M. Yasuda, T. Fujibarshi, I. Shibata, A. Baba, H. Matsuda and N. Sonoda, *Chem. Lett.*, (1955) 167.

[41] D.H. Olson and R.E. Rundle, *Inorg. Chem.*, **2** (1963) 1310.

[42] P. Jutzi, F. Kohl, P. Hofmann, C. Krüger and Y.-H. Tsay, *Chem. Ber.*, **113** (1980) 757.

[43] A.H. Cowley, P. Jutszi, F.X. Kohl, J.G. Lasch, N.C. Norman and E. Schüter, *Angew. Chem. Int. Ed. Engl.*, **23** (1984) 616.

[44] J.L. Atwood, W.E. Hunter, A.H. Cowley, R.A. Jones and C.A. Stewart, *J. Chem. Soc. Chem. Commun.*, (1981) 925.

[45] M.J. Heeg, C. Janiak and J.J. Zuckerman, *J. Am. Chem. Soc.*, **106** (1984) 4259.

[46] D.J. Burkey and T.P. Hanusa, *Organometallics*, **14** (1995) 11.

[47] J.D. Cotton, P.J. Davidson and M.F. Lappert, *J. Chem. Soc. Dalton Trans.*, (1976) 2275.

[48] W. Petz, *Chem. Rev.*, **86** (1986) 1019.

[49] I. Omae, *Organometallic Intermolecular-coordination Compounds*, *J. Organomet. Chem. Lib. 18*, Elsevier, Amsterdam, 1986.

[50] A. Aoki, K, Horiuchi and I. Omae, *Kouen Yokoushu I*, 2F339, p.480, 1995.

[50a] I. Omae, A. Aoki and K. Horiuchi, *Kagaku Kogyo*, in press

[51] *Tin Chemicals, The Formula For Success*, Int. Tin Res. Inst., Publication No. 681, 1987.

[52] R. Hill and A.J. Killmeyer, *Proc. Am. Wood. Preserv. Assoc.*, (1988)131; *Int. Tin Res. Inst. Publication No.* 692, 1988.

[53] *Int. Tin Res. Inst. Publication No.* 665, 1986.

[54] S.J. Blunden and A.H. Chapman, *Organotin Compounds in the Environment*, P.J. Crag ed. Longman, London, 1986; *Int. Tin Res. Inst. Publication No.* 665, 1986.

[55] K. Sakaguchi, *Yoshoku*, April (1988) 118.

[56] K. Schwartz, D.B. Milne and E. Vinyard, *Biochem. Biophys. Commun.*, **40** (1970) 22.

[57] L.R. Sherman, *Silicon Germanium Tin and Lead Compounds*, **9** (1986) 323.

[58] L.R. Sherman, K.I. Bilgicer and N.F. Cardarelli, *J. Nutrit. Growth Cancer*, **2** (1985) 107.

[59] H. Iwai, O. Wada and Y. Arakawa, *J. Anal. Toxicol.*, **24** (1981) 300.

[60] O. Wada, H. Yanagisawa and Y. Kitagawa, *Bunseki*, (1988) 322.

[61] Anon, *J. Amer. Med. Ass.*, **227** (1984) 1450.

[61a] F. Nakakita, *Petrotech*, **16** (1993) 550.

[61b] K. Takahashi, *Toryo Kougaku*, **27** (1992) 107.

[61c] K. Mizuguchi, *Nikkei, New Materials*, March (1990) 3.

[61d] M. Morita, *Kakaku Kogyo*, **40** (1989) 581.

[61e] K. Imaeda, K. Ohsawa and Y. Yoshimura, *Bunseki*, (1988) 432.

[62] C.J. Evans and S. Karpel, *Organotin Compounds in Modern Technology*, *J. Organomet. Chem. Lib. 16*, Elsevier, Amsterdam, 1985.

[63] S.J. Blunden, P.A. Cusack and R. Hill, *The Industrial Uses of Tin Chemicals*, The Royal Society of Chemistry, London, 1985.

[64] M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworth, London, 1987.

[65] I. Omae, *Organotin Chemistry*, *J. Organometallic Chemistry Library 21*, Elsevier, Amsterdam, 1989.

[66] V. Yngve, *U.S. Patent*, 2219463 (1940); *Chem. Abstr.*, **35** (1941) 1145.

[67] *Plastics Age*, Dec. (1996) 133.

[68] S. Karpel, *Tin and its Uses*, No. 158 (1988) 15.

[69] A.H. Frye, R.W. Host and M.A. Paliobagis, *J. Polymer Sci. A*, **2** (1964) 1765.

[70] A.H. Frye, R.W. Host and M.A. Paliobagis, *J. Polymer Sci. A*, **2** (1964) 1785.

[71] A.H. Frye, R.W. Host and M.A. Paliobagis, *J. Polymer Sci. A*, **2** (1964) 1801.

[72] A. Guyot, *Pure and Appl. Chem.*, **57** (1985) 833.

[73] T. Hjietberg and E.M. Sörvik, *Polymer*, **24** (1983) 673.

[74] H. Hjertberg and E.M. Sörvik, *Polymer*, **24** (1983) 685.

[75] R.C. Poller, *J. Macromol. Sci. Chem. A*, **12** (1978) 373.

[76] F. Alavi-Moghadam, G. Ayrey and R.C. Poller, *Eur. Polymer J.*, **11** (1975) 649.

[77] F. Alavi-Moghadam, G. Ayrey and R.C. Poller, *Polymer*, **16** (1975) 833.

[78] F. Hostettler and E.F. Cox, *Ind. Eng. Chem.*, **52**(7) (1960) 609.

[79] J.W. Britain and P.G. Gemeinhardt *J. Appl. Polymer Sci.*, **4** (1960) 207.

[79a] F.W. van der Weij, *J. Polym. Sci. Polym. Chem. Ed.*, **19** (1981) 381.

[79b] F.W. van der Weij, *J. Polym. Sci. Polym. Chem. Ed.*, **19** (1981) 3063.

[79c] J. Otera, T. Yano and R. Okawara, *Chem. Lett.*, (1985) 901.

[80] F.W. van der Weij, *Makromol. Chem.*, **181** (1980) 2541.

[81] M and T Chemicals Inc., *Technical Information Sheet* 277, Catalyst T-l, Dibutyltin diacetate.

[82] W.L. Carrick, R.W. Kluiber, E.F. Bonner, L.H. Wartman, F.M. Rugg and J.J. Smith, *J. Am. Chem. Soc.*, **82** (1960) 3883.

[83] G.J.M. van der Kerk and J.G.A. Luijten, *J. Appl. Chem.*, **4** (1954) 314.

[84] J.G.A. Luijten and G.J.M. van der Kerk, *J. Appl. Chem.*, **11** (1961) 35.

[85] J.G. Noltes, J.G.A. Luijten and G.J.M. van der Kerk, *J. Appl. Chem.*, **1** (1961) 38.

[86] C.J. Evans and P.J. Smith, *J. Oil Col. Chem. Assoc.*, **58** (1975) 160. Int. Tin Res. Inst. Publication No. 505.

[87] I. Hamman, *Nachrichten Bayer*, **31** (1978) 61.

[88] Peropal, *Bayer Agrochemicals Div. Report*, E2-821/843304, 4pp.

[89] B.A. Richardson, *Proc. Am. Wood Presev. Assoc.*, (1988) 56.

[90] S.J. Blunden and R. Hill, *Appl. Organomet. Chem.*, **2** (1988) 251.

[91] R.V. Subramanian, J.A. Mendoza and B.K. Garg, *Holzforsch*, **35**:253.

[92] R.V. Subramanian, J.A. Mendoza and B.K. Garg. *Holzforsch*. **35**:263.

[93] M. Tsuboi, *Kagaku to Kogyo* (*Chemistry and Industry*), **33** (1980) 552.

[94] M. Nakao, *Betsusatsu Kagaku Kogyo*, **29** (1985) 345.

[95] T. Tahara, *Yukikinzoku Polymer* (*Organometallic Polymers*), N. Hagihara and A. Nakamura ed. Gakkai Shuppan Center, Tokyo, p. 101, 1982.

[96] R.V. Subramanian and K.N. Somasekharan, *J. Macromol Sci. Chem.* A **16** (1981) 73.

[97] S. Karpel, *Tin and Its Uses*, **142** (1984) 6.

[98] B. Sugavanam, *Int. Tin Res. Inst. Publication No.* 607, 1981.

[99] A.J. Crowe, *Int. Tin Res. Inst. Publication No.* 679, 1987.

[100] A.-M. Coles, *Tin and Its Uses*, **140** (1984) 12.

[101] F.E. Smith, *Int. Tin Res. Inst. Publication No.* 607, p. 3.

[102] *Manufacturing Chemist*, Nov.(1988) 62.

[103] A.J. Crowe, *Drugs of the Future*, **12**(3) (1987) 255; *Int. Tin Res. Inst. Publication No.* 676.

[104] A.K. Saxena and F. Huber, *Coord. Chem. Rev.*, **95** (1989) 109.

[105] A.J. Crowe, P.J. Smith and G. Atassi, *Inorg. Chem. Acta*, **93** (1984) 179.

[106] A.J. Crowe, P.J. Smith and G. Atassi, *Chem.-Biol. Interactions*, **32** (1980) 171.

[107] G. Atassi, *Rev. Silicon, Germanium, Tin and Lead Compounds*, **8** (1984) 219.

[108] H.A. Meinema, A.M.J. Liebregts, H.A. Budding and E.J. Bulten, *Rev. Silicon Germanium Tin and Lead Compounds*, **9** (1985) 157.

[109] A.M. Crowe and P.J. Smith, *Int. Tin Res. Inst. Publication No.* 583 (1980) 60.

[110] A.J. Crowe and P.J. Smith, *Chem. Ind.*, March (1980) 200.

[111] M. Gielen, R Willem, T. Mancilla, J. Ramharter and E. Joosen, *Silicon Germanium Tin and Lead Compounds*, **9** (1986) 349.

[112] S.G. Ward, R.C. Taylor and A.J. Crowe, *Appl. Organomet. Chem.*, **2** (1988) 47; *Int. Tin Res. Inst. Publication No.* 693.

[113] N.F. Cardarelli, *Silicon Germanium Tin and Lead Compounds*, **9**(4) (1986) 307.

[114] A.H. Penninks, P.M. Punt, M. Bol-Schoenmakers H.J.M. van Rooijen and W. Seinen, *Silicon Germanium Tin and Lead Compounds*, **9**(4) (1986) 367.

[115] A.J. Crowe, P.J. Smith, C.J. Parge and F.E. Smith, *Cancer Lett.*, **24** (1984) 45.

[116] G. Ruisi, A. Silvestri, M.T. Lo Giudice, R. Barbieri, G. Atassi, F. Huber, K. Gratz and L. Lamartina, *J. Inorg. Biochem.*, **25** (1985) 229.

[117] T. Suzukawa, *Seramikkusu* (*Ceramics*), **4** (1969) 852.

[118] S. Karpel, *Tin and its Uses*, No. 157 (1988)12.

11 Organolead Compounds

11.1 INTRODUCTION

Lead is in the same group 14 as silicon, germanium and tin. The amount produced is very large compared with the other elements, and thus it is a low price metal. An organolead compound was prepared by Löwig [1] in 1853, and the use of it rapidly increased since Midgley and Boyd [2] found in 1922 that tetraethyllead is an excellent antiknock agent. In the 1970s, tetraethyllead was produced in large amounts (more than 650 thousand tons per year) in the world [3]. But recently, exhaust fumes from automobiles have caused public discussion. The regulation of the amount added to gasoline has become gradually more rigorous and its consumption has decreased sharply. Organolead compounds in general have high reactivities, the metal as a raw material is cheap, and we may expect the development of new uses.

11.2 LEAD

Galena (lead sulfide, PbS, Pb 86.6 %), alglesite ($PbSO_4$, Pb 68.3 %) and cerussite (white lead ore, $PbCO_3$, Pb 77.5 %) are the main ores of lead. These ores are calcined to give lead oxide (PbO) [4], and crude lead is prepared by reduction with coke in a smelting furnace. The crude lead is electrolyzed with a hexafluorosilicate ($PbSiF_6$) and hexafluorosilicic acid (H_2SiF_6) as electrolytes to give 99.997 % or more high purity lead on cathode [5]. As the anode sludge contains Au, Ag and Cu, etc., these metals are recovered by other treatments as byproducts [6].

Lead has a low melting point, a high specific gravity, softness, malleability and is an easily processed element. A fresh cut or cast lead surface undergoes oxidation and tarnishes rapidly to form the insoluble protective layer of basic lead carbonate. Lead is not eroded in air, in water and in soil because of this protective layer.

Lead metal resists hydrochloric acid, highly concentrated sulfuric acid and hydrofluoric acid, but it dissolves readily in warm, dilute nitric acid. Lead is also corroded by weak organic acids such as acetic acid or tartaric acid in the presence of oxygen [7].

Lead is an essential commodity in the modern industrial world, ranking fifth in tonnage consumed after iron, copper, aluminum and zinc. In 1995, lead production in the world was estimated to be 5.3×10^6 tons [7,7a]. 50 % or more of the use of lead is in the storage battery. Next are pigments and chemicals. The pigments are

Table 11.1 Physical properties of lead [4,7]

Property	Value
atomic weight	207.2
melting point, °C	327.4
boiling point, °C	1770
specific gravity, g/cm^3, 20 °C	11.35
specific heat, J/(kg.K)	130
thermal conductivity, relative to Ag = 100	8.2
electrical conductivity, relative to Cu = 100	7.8
magnetic susceptibility, H m^{-1}kg^{-1}, 20 °C	-1.5×10^{-9}
Brinell hardness, 20 °C	2.5–3.0
Young's modulus, GPa	16.5
elongation (in 5-cm gauge length), %	50–60

lead cyanide ($Pb(CN)_2$, corrosion-proof pigment), red lead (Pb_3O_4) and white lead ($2PbCO_3{\cdot}Pb(OH)_2$). Chemicals are lead dioxide (PbO_2, used for electrode, curing agent for polysulfide type rubbers), lead azide ($Pb(N_3)_2$, an initiating explosive), lead borate ($Pb(BO_2)_2$, drying agent for varnish and paints), lead carbonate ($PbCO_3$, PVC stabilizers, additives for high pressure lubricant greases) and organolead compounds described below [6,7]. The third are semifinished products rolled and extruded lead, mainly sheet and pipe. Piping was formerly the greater part of this sector, but toxicity concerns and substitution by plastics and copper have reduced the market considerably. The uses of lead sheet for roofing, restoration of old buildings, sound insulation, radiation shielding, and chemically resistant linings are now greater than that for piping and are growing steadily [7]. The fourth, alloys, are solders (50–60% Sn), type metal (2.5–12% Sn, 2.5–25% Sb) and bearing alloys (10–15% Sb, 5–10% Sn), etc. Type metal usage has nearly disappeared. Uses of lead-base solder are growing, as electronic products find increasing markets [7]. The fifth is cable sheathing. A major area was in the protection of electrical and telecommunication cables, but this market has declined drastically since the early 1960s due to substitution by aluminum and plastics [7].

Miscellaneous uses are wheel weights, yacht keels, ornamental items, etc. [7].

11.3 PREPARATION OF ORGANOLEAD COMPOUNDS

Organolead compounds are prepared industrially by an electrolysis process. As the alloy process is the first synthetic reaction of organolead compounds, found by Löwig [1], Shapiro named it the Löwig process at the Symposium of Metal-Organic Compounds in 1957 [8]. It is the reaction of a sodium–lead alloy with organic halides.

$$4NaPb + 4RCl \longrightarrow R_4Pb + 4NaCl + 3Pb \qquad (11.1)$$

For example, EtCl reacts with the alloy to give tetraethyllead in 85 % yield [9]. This method is such that only one quarter of the lead is converted to lead alkyl and the remainder has to be recycled. Unfortunately, sodium-rich alloys such as Na_4Pb do not react satisfactorily. Ketones, aldehydes, acetals, acid anhydrides, esters, amides, phosphoric acid esters, organosilicons, organoaluminum compounds, etc. as reaction accelerators of the alloy process have been reported [9]. For example, the reaction of EtCl at 100–120 °C in the presence of 0.1 % acetone gives tetraethyllead in 98 % yield [10].

The electrolysis process was developed in the 1950s by Karl Ziegler [11,12]. The process is carried out with an anode of Pb, a cathode of mercury, and the electrolyte is sodium aluminum tetraethyl ($NaAlEt_4$). As shown in Scheme 11.1 [11], ethylene and hydrogen besides Pb (the anode) are added to the reaction system. Et_4Pb is produced at the anode. Na forms at the anode, and it reacts with hydrogen to give NaH. The NaH reacts with ethylene and Et_3Al, which is produced as the anode, to reproduce the $NaAlEt_4$. The electrolysis process results in Et_4Pb being produced with a high yield of 96–97 % and it does not require the recycling of Pb. Only 3–4 % of ethane or butane are yielded as byproducts [13].

$$\begin{array}{l}
4NaAlEt_4 + Pb \longrightarrow 4Na + Et_4Pb + 4Et_3Al \\
4Na + 2H_2 \longrightarrow 4NaH \\
4NaH + 4Et_3Al + 4C_2H_4 \longrightarrow 4NaAlEt_4 \\
\hline
Pb + 2H_2 + 4C_2H_4 \longrightarrow Et_4Pb
\end{array}$$

Scheme 11.1 [11]

The other electrolysis process uses Grignard reagents as raw materials. Pb is used as an electrode. Grignard reagents react with an alkyl chloride in the tetrahydrofuran or triethyleneglycolbenzylether as a solvent. The control of reaction conditions suppresses the Wurtz type side reactions. R_4Pb is produced in a yield of 90 % or more [3].

$$2RMgCl + 2RCl + Pb \longrightarrow R_4Pb + 2MgCl_2 \quad (11.2)$$

Organolead compounds are prepared with Grignard reagents, organoaluminum compounds or organolithium compounds in laboratories.

The reaction with Grignard reagents yields a liable R_2Pb as an intermediate, which in turn immediately gives R_6Pb_2 and Pb by a disproportionation reaction and furthermore the disproportionation of R_6Pb_2 yields R_4Pb and Pb. R_4Pb is produced in 60–80 % yield as shown in Scheme 11.2 [9,11]. If R is bulky, the reaction stopped at the R_6Pb_2 stage. If R is phenyl, R_6Pb_2 or R_4Pb is produced, according to the reaction conditions. If the Grignard reagents are in excess, R_4Pb tends to be formed. R_6Pb_2 reacts with halogen to give the monohalide, and furthermore the

$$6PbX_2 + 12RMgX \longrightarrow 6R_2Pb + 12MgX_2$$

$$6R_2Pb \longrightarrow 2R_6Pb_2 + 2Pb$$

$$2R_6Pb_2 \longrightarrow 3R_4Pb + Pb$$

$$6PbX_2 + 12RMgX \longrightarrow 3R_4Pb + 3Pb + 12MgX_2$$

Scheme 11.2 [11]

reaction of the monohalide with Grignard reagents yields R_4Pb as shown in eqs. (11.3) and (11.4) [9,11].

$$R_6Pb_2 + X_2 \longrightarrow 2R_3PbX \qquad (11.3)$$

$$R_3PbX + RMgX \longrightarrow R_4Pb + MgX_2 \qquad (11.4)$$

The Grignard reaction, with the addition of organic halides, improves the yields without the precipitation of Pb as shown in eq. (11.5) [3,9,14]. The Grignard reaction with $Pb(OAc)_4$ in the THF as a solvent give R_4Pb in high yield [3,9,15].

$$2RMgCl + RX + PbCl_2 \longrightarrow R_4Pb + 2MgCl_2 + 2MgXCl \qquad (11.5)$$

$$4RMgCl + Pb(OAc)_4 \longrightarrow R_4Pb + 4MgCl(OAc) \qquad (11.6)$$

R = Et, Yield = 94 %

Reactions with organoaluminum compounds or organolithium compounds yield Pb as shown in eqs. (11.7) and (11.8). However, the reactions with organic halides also improve the yields without the formation of Pb as shown in eqs. (11.9) and (11.10) [6,16]. Furthermore the reaction with $Pb(Oac)_4$ and Et_3Al in toluene as a solvent also gives Et_4Pb in high yield as shown in eq. (11.11) similar to the reaction shown in eq. (11.6) [14].

$$6PbX_2 + 4R_3Al \longrightarrow 3R_4Pb + 3Pb + 4AlX_3 \qquad (11.7)$$

$$2PbX_2 + 4RLi \longrightarrow R_4Pb + Pb + 4LiX \qquad (11.8)$$

$$PbCl_2 + R_3Al + RX \longrightarrow R_4Pb + AlX_3 \quad (11.9)$$

$$PbCl_2 + 3RLi + RX \longrightarrow R_4Pb + 2LiCl + LiX \quad (11.10)$$

$$3Pb(OAc)_4 + 4Et_3Al \longrightarrow 3Et_4Pb + 4Al(OAc)_3 \quad (11.11)$$

11.4 PROPERTIES OF ORGANOLEAD COMPOUNDS

Lead is located in group 14 of the periodic table. The element displays valences of +2 and +4. The various inorganic lead compounds are mostly +2 and it is thought to be an ionic bond. On the other hand, organic lead compounds form mostly covalent bonds of four valence. The divalence of organolead compounds is liable. They are difficult to isolate at ordinary temperatures. In the case of Ph_2Pb, it disproportionates to Ph_6Pb_2 and Pb as shown in eq. (11.12). $Pb(C_5H_5)_2$, C_5H_5PbX (X = Cl, Br, I, OAc) and $Pb(CHSiMe_3)_2$ are known as divalent organolead compounds [3].

$$Ph_2Pb \longrightarrow [[Ph_2Pb]_n] \longrightarrow Ph_6Pb_2 + Pb \quad (11.12)$$

The coordination number of lead is 4 to 8: some examples are shown in Figure 11.1 [3,17–21].

Electronegativity, covalent bond radii, bond length of M-C and M-H and dissociation energies of M-C, M-H and M-M of group 14 elements are shown in Table 11.2 [9,11,22,22′]. The covalent bond radii of M, bond length of M-C and M-H increase in proportion to the atomic number from C to Pb. In contrast, the dissociation energies of M-C, M-H and M-M bond decrease, namely, the M-C, M-H

Table 11.2 Some physical data of group 14 M-C, M-H, and M-M bonds [11,9,22,22′]

M	C	Si	Ge	Sn	Pb
electronegativity	2.50	1.74	2.02	1.72	1.55
covalent radius (Å)	0.772	1.176	1.225	1.405	(1.750)
length of bonds (Å)					
M-C	1.54	1.95	1.99	2.17	2.29
M-H	1.07	1.48	1.52	1.70	1.82
energy of dissociation (kcal/mol)					
M-C	83	70	59	50–52	37
M-H	99	75	74	71	–
M-M	83.1	42.2	37.6	34.2	23

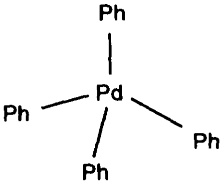
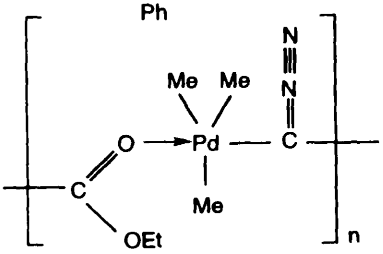
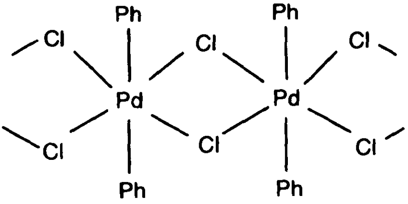
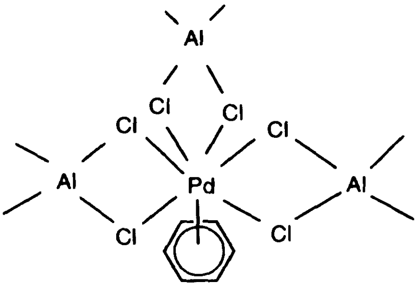
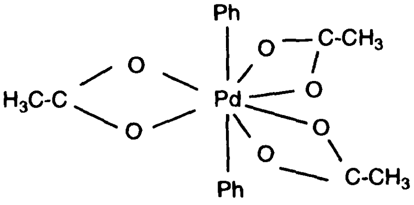
Coordination number		Structure	Pd-C bond length Å
4	tetrahedral		2.19
5	trigonal bipyramidal		2.177
6	octahedral		2.12
7	pentagonal bipymidal		3.11
8	hexagonal bipyramidal		2.16

Figure 11.1 Structure of organolead compounds [17–21].

and M-M bonds of organolead compounds are weak and liable, and thus many organolead compounds decompose by heating up to 100–200 °C.

Tetravalent organolead compounds are generally stable at room temperatures, and lower tetraalkylleads can be distillated under reduced pressure. Organolead compounds are stable to water and they are also stable to oxygen in air [9]. The order of thermal stability of R_4Pb is Ph > Me > Et > *iso*-Pr [23]. Pb-C bonds are easily decomposed by halogens, strong oxidizing agents, and acid anhydrides [9]. The stability of $R_3Pb\text{-}PbR_3$ is lower than R_4Pb. The organolead in compounds having a Pb-Pb-Pb bond or a more metal–metal bond are not known as organosilicon, organogermanium and organotin compounds [24]. As monohalides (R_3PbX) decompose partly at room temperatures, they need to be stored in a cool dark place. The order of stabilities of R_3PbX regarding R and X are as follows:

$$\text{aryl} > \text{alkyl}, \qquad F > Cl > Br > I.$$

The decomposition of R_3PbX at first yields R_2PbX_2 by a disproportionation, then decomposes to $RPbX_3$, and finally becomes RX and PbX_2 as shown in Scheme 11.3 [3].

$$2R_3PbX \longrightarrow R_4Pb + R_2PbX_2$$

$$2R_2PbX_2 \longrightarrow R_3PbX + RPbX_3$$

$$RPbX_3 \longrightarrow RX + PbX_2$$

Scheme 11.3 [3]

R_3PbX yields hydride R_3PbH by reduction with $LiAlH_4$ or KBH_4 [3,24]. With the hydride, hydroplumbylation of hydrometalation proceeds similarly as in the reaction of organometallic hydrides of Si, Ge and Sn [3,25,26].

Tetraethyllead and tetramethyllead are highly toxic. Therefore, inhalation of and touch with these should be avoided. If these organolead compounds touch the skin, wash the skin with kerosene or petroleum ether within 15 minutes, then wash with soap and water thoroughly [9].

$$Bu_3PbH + CH_2{=}CHCOOMe \longrightarrow Bu_3PbCH_2CH_2COOMe \tag{11.13}$$

11.5 APPLICATIONS OF ORGANOLEAD COMPOUNDS

11.5.1 ANTIKNOCK AGENTS

The representative use of organolead compounds is as an antiknock agent which suppress knocking of internal-combustion engines. First of all, the author will describe on the phenomenon of knocking. In the internal-combustion engines of spark ignition, if compression ratio increases, the generated power increases. But a certain compression ratio shows the maximum power generation. The generated power decreases even if the compression ratio further increases because the phenomenon of knocking arises, i.e. knocking arises when the compression ratio is too high. Usually, fuel is ignited when fuel is compressed by a piston, and the combustion of fuel starts, fire successively propagates, and the whole fuel burns. But, if the compression ratio is too high, unburned fuel becomes a pressure-high state by expansion of the burnt gas when a part of fuel burns, and the remaining fuel is to be autoignited. If the autoignition arises besides the natural burning, gas vibration of high frequency occurs, and metallic noise, the loss of heat efficiency, the increase of abrasion, and the damage of piston also occur. These phenomena are called knocking [27,28].

Antiknock agents are substances to inhibit autoignition caused by oxidative chain reaction under high pressure [27]. Namely, they are substances to act as radical scavengers which act to stop the chain reaction caused by radicals. Therefore, branched alkyl or aromatic compounds which tend to yield stable radicals, act as radical scavengers of highly reactive radicals such as $H\cdot$ or $CH_3\cdot$ and they act to suppress knocking. Therefore, they are used for high octane number fuels.

Octane number is measured by research. The octane number of hexane is 24.9, branched alkane; *iso*butane is 101.3 and 2,3,4-trimethylpentane is 102.5, in aromatic compounds; benzene is 106, toluene is 110 [28,29]. These compounds having high octane numbers are used for blending agents to gasoline.

The other blending agents used are TBA (tert-butyl alcohol; octane number 108) and MTBE (methyl tert-butyl ether; octane number is 115), etc. [29]. MTBE is produced by the reaction of isobutylene with methyl alcohol in the presence of an ion-exchange resin as a catalyst [29]. The production of MTBE increased from the latter half of the 1970s as the blending agent in place of tetraethyllead, in 1989 it accounted for 7.425 million tons throughout the world, in 1991 the production is over 10 million tons, in 1994 the production is sharply over 20 million tons [30,30d]. These blending agents of alcohol or ethers act to decrease the amounts of carbon monoxide and hydrocarbon in the exhaust gas, therefore these are good for environmental problems.

Tetraethyllead (bp about 200 °C [31], 91 °C/19 mmHg [32]) is the representative antiknock agent: the octane number increases by 10–15 when 0.8–1.0 g per one liter of gasoline is added to gasoline. It is the lowest price substance as an antiknock agent [29]. Tetramethyllead (Me_4Pb, bp 100 °C [32]) is a lower boiling point substance than tetraethyllead, and is also excellent antiknock agent. These mixture or these disproportionation products (Et_3PbMe, Et_2PbMe_2, $EtPbMe_3$) are also used as antiknock agents [29].

Tetramethyllead provides good blending with the lighter component of a gasoline since tetramethyllead is a low boiling point substance. The mixture of TEL and TML provides more even distribution of antiknock quality throughout the gasoline boiling range since they are mixed with the lighter component. Hence, actually, not one component of tetraethyllead but these mixture with tetramethyllead and disproportionation products are used as antiknock agents [29].

The action of organolead compounds as an antiknock agent have not been completely elucidated yet. But organolead compounds are thought to act as the scavenger of peroxy radicals which are generation source of autoignition caused under high pressures. It is thought that, actually, the decomposed fine foggy lead oxide acts as a radical scavenger [3,9,33]. BCH_2CH_2Br or $ClCH_2CH_2Cl$ is added as an additive to gasoline besides organolead compounds. They act as chemical scavengers to remove the small amount of lead compounds that might remain in the engine after combustion of the fuel. These scavengers contains chlorine and/or bromine to convert the lead compounds of lead chloride and or lead bromide which are gaseous at the temperatures prevailing inside an engine ($PbBr_2$ (bp 918 °C), $PbCl_2$ (bp 950 °C) [9].

The antiknock agents of organometallic compounds are shown in Figure 11.2 [33a,33b]. MMT (methylcyclopentadienylmanganese tricarbonyl) and iron pentacarbonyl are used, besides tetraethyllead. Iron pentacarbonyl and ferrocene had been used before tetraethyllead used in the 1930s. MMT have published in 1957 by Ethyl Corporation, which is as the same or more effective antiknock agent for tetraethyllead. A small amount of MMT was used in the United States since it was expensive. However, from 1975, MMT as an antiknock agent for unleaded gasoline had increased rapidly. In 1978, however, MMT was banned from use in United States unleaded gasoline on a suspicion that it may increase exhaust gas emissions. But, it is preferable for environmental problems from the exhaust gas of cars since the use of MMT decreases sharply the amount of NOx compared with the usual exhaust gas. A small amount of Mn_3O_4 exhaused, is not toxic by human and animals consumption and it does not effect to catalytic converters [34]. Therefore, MMT have been used in Canada since 1977. Afterward, Ethyl Corporation sued the inhibition of use at a court of United States and won the case in April 1994. But, as EPA reserved the registration of MMT, in September 1995, the court decided EPA should register MMT at once and Ethyl Corporation started to sell in United States since December 1995.

Organolead compounds such as $(CH_2{=}CH)_4Pb$, Et_3PbI, and organometallic compounds of thallium, selenium and tellurium have been reported as the other antiknock agents [9,27]. Now, catalytic converters are attached for exhausted gas. These uses are more difficult because deterioration of catalyst of the converter increases.

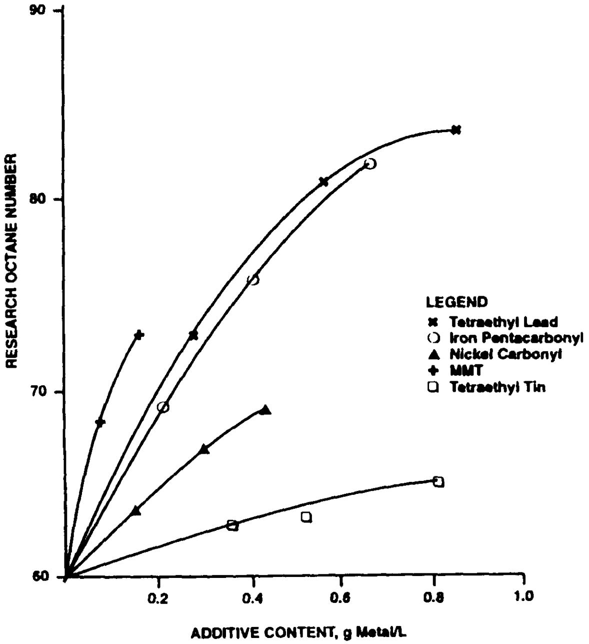


Figure 11.2 Effectiveness of organometallic antiknock additives [33a,33b]

In United States, the additive amount of organolead compounds to gasoline was the highest, 0.653 g/l in 1958–1969. The consumption was the largest, 312×10^3 tons per year. But afterwards, since the toxicity of exhaust gases of automobiles became a public issue, the compression ratios of engines were reduced, with the intention of decreasing the amount of exhaust gases. The gasoline octane number requirement was also moderated to reduce the added amount of organolead compounds in the gasoline. Furthermore, the added amount of organolead compounds decreased since catalytic converters were attached in 1974. In 1978, the amount of addition is 0.391 g/l. Consumption of organolead compounds decreased to 205×10^3 tons/year. Further, EPA (Environmental Protection Agency) regulated to 0.132 g/l and the consumption of organolead compounds decreased to 87×10^3 tons/year [35] and further regulated to 0.026 g/l [36].

In Japan, in 1970 exhaust gas of cars became a social problem. In 1975, the regulation of exhaust gases started. In September 1987 substantially completely unlead gasoline started in Japan [36]. On the other hand, in the regulation of exhaust gas, Europe lags behind United States. Asian countries, besides Japan, further delay in the regulation. As the regulation of each country is different, the use of organolead compounds is clearly not known. If the gasoline is used with the average value of the regulation, in 1989, the consumption of organolead compounds is estimated 190×10^3 tons in the world [7,36–38]. Further, each counties clamp regulation year by year and it is estimated the consumption of organolead compounds should have decreased.

11.5.2 POLYMER CATALYSTS

If organolead compounds are heated, the radicals are easily produced by a decomposition. Organolead compounds have been investigated as the polymerization initiators of various kinds of unsaturated compounds [9,10,39,40]. The unsaturated compounds are ethylene, propylene, butadiene, styrene, acrylonitrile and vinyl chloride, etc. Organolead compounds are tetraethyllead, tetracyclohexyllead, tetravinyllead, tetraethyllead and $TiCl_3$, the mixtures with organoaluminum compounds or transition metal halides [9,10,39,40].

For example, polymerization of ethylene or propylene at 200–400 °C, 1–250 atm gives only liquefied polymers. However, with Ziegler type catalysts of tetraethyllead and metal halides (halides of Ti, Mo or V), produces the polymerization at 90–180 °C form an atmospheric pressure to a high pressure gives crystalline polymers [39]. Organolead compounds have been investigated as catalysts for polyesters, polysulfones, polyurethanes, etc. [9,39].

11.5.3 DISINFECTANTS AND INSECTICIDES

Trialkyl organolead compounds have a disinfectant action similar to organogermanium and organotin compounds. The action of disinfectant is stronger than for the organogermanium compounds and almost similar to that for organotin compounds. Propyl group to gram-negative bacteria, butyl or pentyl groups to gram-positive bacteria, showed the strongest disinfectant action as shown in Table 11.3 [9].

Organolead compounds are available for agrochemicals such as insecticides and herbicides [9]. But the investigation research is few since organolead compounds have high toxicities. For example, $Et_3PbN(sec\text{-}Bu)_2$ is a herbicide. Triethylphthalohydrazidelead is effective to the brown rot of potatoes and the rottenness of peach. Tri type of organolead compounds is able to be used for antifouling paints or wood preservatives [10].

11.5.4 MISCELLANEOUS USES

If organolead compounds are heated at high temperatures, thin film forms on the metal surface. Therefore, they are able to be used in electroless deposition [9,40]. The others are able to be used as PVC stabilizers [10,22,40] and antioxidants [40].

Table 11.3 Minimal concentration (ppm) causing complete inhibition of visible growth on peptone glucose agar [9]

compound $R(R_3PbOAc)$	fungi			
	Botrytis allii	Penicillium italicum	Aspergillus niger	Rhizopus nigricans
methyl	100	200	200	> 500
ethyl	20	20	20	50
propyl	2	5	10	5
butyl	0.1	0.5	0.5	0.5
iso-butyl	0.1	0.2	0.5	0.5
pentyl	0.1	0.2	0.5	0.5
iso-pentyl	0.1	0.2	0.2	0.5
hexyl	0.5	2	2	100
heptyl	50	100	100	> 500
octyl	> 500	> 500	> 500	> 500
phenyl	2	2	2	5

compound $R(R_3PbOAc)$	bacteria			
	gram-positive		gram-negative	
	Bacillus subtilis	Mycobacterium phlei	Escherichia coli	Pseudomonas fluorescens
methyl	100	100	200	100
ethyl	50	50	50	20
propyl	2	2	5	10
butyl	0.5	0.5	20	20
iso-butyl	0.5	0.05	20	50
pentyl	0.5	0.1	50	50
iso-pentyl	0.5	0.2	50	50
hexyl	5	0.2	> 500	> 500
heptyl	20	5	> 500	> 500
octyl	50	20	> 500	> 500
phenyl	1	0.05	20	50

REFERENCES

[1] C. Löwig, *Liebigs Ann. Chem.*, **88** (1853) 304; *J. Prakt. Chem.*, **60** (1853) 304.

[2] T. Midgley, Jr. And T.A. Boyd, *J. Ind. Eng. Chem.*, **14** (1922) 894;
T. Midgley, Jr., C.A. Hochwalt and G. Calingaert, *J. Am. Chem. Soc.*, **45** (1923) 1821.

[3] P.G. Harrison, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 2, p. 629, 1982.

[4] Kirk-Othmer, *Concise Encyclopedia of Chemical Technology*, Wiley, New York, p. 688, 1985.

[5] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, p. 291, 1987.

[6] *11290 no Kagaku Shohin*, Kagaku Kogyo Nipposha, Tokyo, p. 107, 1990.

[7] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, Vol. A15 p. 193, 1990.

[7a] *Kogyo Binran*, Tsusho Sangyo Chosakai Shuppanbu, 1997.

[8] H. Shapiro, *Metal-Organic Compounds*, American Chemical Society, p. 290, 1959.

[9] L.W. Willemsens, *Organolead Chemistry*, International Lead Zinc Research Organization, New York, 1964.

[10] J.H. Harwood, *Industrial Applications of Organometallic Compounds*, Chapman and Hall, London, p. 124, 1963.

[11] W.P. Neumann and K. Kühlein, *Ad. Organomet. Chem.*, **7** (1968) 241.

[12] K. Ziegler and Lehmkuhl, *Angew. Chem.*, **67** (1955) 424.
K. Ziegler, *Angew. Chem.*, **71** (1959) 628;*72* (1960) 565.

[13] *Chem. Eng. News*, **37** (24) (1959) 22.

[14] F.W. Frey, Jr. And S.E. Cook, *J. Am. Chem. Soc.*, **82** (1960) 530.

[15] K.C. Williams, *J. Org. Chem.*, **32** (1967) 4062.

[16] H. Gilman, L. Summers and R.W. Leeper, *J. Org. Chem.*, **17** (1952) 630.

[17] V. Busetti, M. Mammi, A. Signor and A. Del. Pra, *Inorg. Chim. Acta*, **1** (1967) 424.

[18] M. Birkhahn, E. Glozbach, W. Massa and J. Lorberth, *J. Organomet. Chem.*, **192** (1980) 171.

[19] M. Mammi, V. Busetti and A. Del Pra, *Inorg. Chim. Acta*, **1** (1967) 419.

[20] A.G. Gash, P.F. Rodesiler and E.L. Amma, *Inorg. Chem.*, **13** (1974) 2429.

[21] N.W. Alcock, *J. Chem. Soc. Dalton Trans*, (1972) 1189.

[22] L.C. Willemsens and G.J.M. van der Kerk, *Investigations in the Field of Organolead Chemistry*, International Lead Zinc Research Organization, 1965.

[22′] A. Bondi, *J. Phys. Chem.*, **68** (1964) 441.
Kagakubinran, Japan Chemical Society ed., Maruzen, 1984.
M. Wada, *Kagaku*, **26** (1971) 131.
R.C. Poller, *The Chemistry of Organotin Compounds*, Logos Press, London, 1970.
G.E. Coats, M.L. Green, P. Powell and K. Wade, *Principles of Organometallic Chemistry*, Methuen, 1968.
H.A. Skinner, *Advances in Organometallic Chemistry*, Academic Press, New York, 1964.
F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience Publ., 1962.

[23] Ch. Elschenbroich and A. Salzer, *Organometallics*, VCH, Weinheim, p. 137, (1989)

[24] G.E. Coates, M.L.H. Green and K. Wade, *Organometallic Compounds, Vol. 1, The Main Group Elements*, Methuen, London, 1967.

[25] W.E. Becker and S.E. Cook, *J. Am. Chem. Soc.*, **82** (1960) 6264.

[26] W.P. Neumann and K. Kühlein, Angew. Chem., **77** (1965) 808.

[27] *Sekai Kagaku Daijiten (Encyclopedia of Science and Technology, Technopia)* Kodansha, Tokyo, Vol. 1, p. 197, 1985.

[28] *Kagaku Binran, Oyohen*, Japan Chemical Society ed., Maruzen, Tokyo, p. 466, 1980.

[29] Kirk-Othmer, *Encylopedia of Chemical Technology*, John Wiley, vol. 11, p. 652, 1980.

[30] *Kagaku Kogyo Jiho*, 15, 1990.

[30a] J. Mizoguchi, Kagaku Keizai, (1995) 170.

[31] *The Merck Index*, 10th ed., p. 5221, 1983.

[32] G.E. Coates, *Organo-Metallic Compounds*, Methuen, London, p. 201, 1960.

[33] A. Ross and E.B. Rifkin, *Ind. Eng. Chem.*, **48** (1956) 1528; E.B. Rifkin and C. Walcutt, *Ind. Eng. Chem.*, **48** (1956) 1532.

[33a] K. Owen and T. Coley, *Automotive Fuels Reference Book*, 2nd ed., Society of Automotive Engineers, Inc., 1995.

[33b] J.J. Russel, Motor Gasoline Antiknock Additives, Associated Octel Company Report 87/10 1987.

[34] P.J. Abbott, *Science Total Environment*, **67** (1987) 247.
[35] Kirk-Othmer, *Encylopedia of Chemical Technology*, John Wiley, vol.14, p. 191, 1980.
[36] T. Osawa, *Nisseki Review*, **27** (5) (1985) 294.
[37] *British Petroleum Statistical Review*, 1990.
[38] *CONCAWE, Report no 2*, 1990.
[39] R.L. Milde and H.A. Beatty, *Metal-Organic Compounds*, American Chemical Society, p. 306, 1959.
[40] R.W. Leeper, L. Summers and H. Gilman, *Chem. Rev.*, **54** (1954) 101.

12 Organotitanium Compounds

12.1 INTRODUCTION

Speaking of titanium, it is well known that it is used in aircraft materials, golf clubs, tennis rackets, the rim of spectacles, etc., since it is light and has a high tensile strength. Titanium white (TiO_2) of a white pigment, $TiCl_3$ or $TiCl_4$ for Ziegler-Natta catalysts as inorganic titanium compounds, and further titanium alkylesters ($Ti(OR)_4$) of water repellent for fibers as organic titanium compounds, are also well known. However, titanium is different from the elements described up to here, since titanium is a transition element. Organotitanium compounds are not familiar, especially alkyltitaniums are not known since they are liable. This chapter mainly describes on applications for organosynthetic use which recently came to public notice.

12.2 TITANIUM

Titanium is an element of group 4 of the periodic table. It is in the same group as zirconium and hafnium. It has a high similarity to silicon which was the same group in the old periodic table. Titanium exists in 5600 ppm in the Earth's crust [1], it is the fourth largest element after iron, aluminium and magnesium as common use metal. The titanium deposits are approx. 340 million tons or more [2]. The span of life as a metal resource is three thousand years or more, the ranking of the life of resources as practical metals is the second after iron.

Rutile (TiO_2) and ilmenite ($FeO{\cdot}TiO_2$) are used as the ores of titanium. The ilmenite is required to remove iron since it is a solid solution of magnetic iron ore and titanium oxide. There are two processes in the refining process to remove iron from the ilmenite.

The first method is that the ilmenite is mildly reduced with a solid reducing agent, iron is removed by a magnetic separation, furthermore the remaining iron was completely percolated with sulfuric acid, filtrated, dried, fractionated and calcined to give a synthetic rutile (TiO_2, 95 %).

The second is that the iron oxide of the ilmenite is reduced to give iron metal with carbon in the electric furnace and titanium oxide is obtained as titanium slug with a high content.

Titanium is produced by chlorination of rutile (TiO_2, 95 %), synthetic rutile prepared from ilmenite or titanium slug of a high content with cokes at 1000 °C to give crude $TiCl_4$, which is then purified by distillation and by reduction of the purified $TiCl_4$ with Mg at about 900 °C under argon atmosphere (Kroll process), or by two step reduction with sodium metal (Hunter process) [2–5].

$$TiO_2 + 2Cl_2 + C \longrightarrow TiCl_4 + CO_2 \qquad (12.1)$$

$$TiCl_4 + 2Mg \xrightarrow{900\ ^\circ C} Ti + 2MgCl_2 \qquad (12.2)$$

$$TiCl_4 + 2Na \xrightarrow{120\text{-}130\ ^\circ C} TiCl_2 + 2NaCl \qquad (12.3)$$

$$TiCl_2 + 2Na \xrightarrow{900\ ^\circ C} Ti + 2NaCl \qquad (12.4)$$

Titanium is mostly used as a pigment in TiO_2. Therefore, the titanium oxide is directly produced by the following sulfuric acid process and chlorination process from titanium ores. The sulfuric acid process is the process to remove iron in the ilmenite as a solid iron sulfate with sulfuric acid.

The chlorination process is to remove iron as a solid $FeCl_3$ with chlorine from ilmenite. Titanium oxide is produced from ilmenite as the raw materials. However, it is also produced from rutile by oxidation after purification as $TiCl_4$ with chlorination process [2].

Physical properties of titanium compared with the other metals are shown in Table 12.1 [2,3,5a]. The melting point is at 1668 °C and it is slightly higher than that of iron. The specific gravity is small, 4.5 and this corresponds to 60 % of that of iron and about 1.7 times that of aluminum. The coefficient of thermal expansion is 1/2 that of stainless steel (18–8) and $\frac{1}{3}$ that of aluminum. Titanium resists to nitric acid, dilute hydrochloric acid, aqua regia (nitrohydrochloric acid), chromic acid, sea water, wet chlorine gas, hydrogen sulfide, sulfurous acid gas, acetic acid, caustic soda, etc. [3]. Especially, the resistance to sea water is equivalent to that of platinum [6]. The tensile strength per unit weight is two times that of iron, three times that of aluminum and the strength does not change at relatively high temperatures (300–400 °C), and it has a high corrosion resistance.

Therefore, it is used for the airframe of aircrafts, engine parts, heat exchangers in chemical instruments, reaction vessels, electrodes, car parts, construction and building materials, marine development materials, sea water to fresh water desalination plant, golf clubs, tennis rackets, spectacle frames, etc. [2,3,5].

Table 12.1 Comparison of physical properties of titanium with other metals [2,3,5a]

Property	Ti	Fe	Stainless Steel†	Al	Mg	Ni	Cu
specific gravity	4.5	7.9	7.9	2.7	1.7	8.9	8.9
melting point (°C)	1668	1539	1400–1420	660	650	1455	1083
coefficient of thermal expansion (10^{-6}/°C)	8.4	12	17	23	25	15	17
specific heat (cal/gr/°C)	0.124	0.11	0.12	0.21	0.24	0.11	0.092
thermal conductivity (cal/cm^2/sec/°C/cm)	0.041	0.15	0.039	0.49	0.38	0.22	0.92
electrical resistance (μohm-cm)	55	9.7	72	2.7	4.3	9.5	1.724
electrical conductivity (%IACS)	3.1	18	2.4	64	40	18	100
Young's Modulus (kgf/mm^2)	10 850	21 000	20 400	7 050	4 570	21 000	11 000
Poisson's ratio	0.34	0.31	0.3	0.33	0.35	0.30	0.34
tensile strength (kgf/mm^{-2})	3.8	22	63–105	4.76	15.0	32.2	21.7
(purity, %)	99.9	99.9	—	99.99	99.9	99.95	99.95

†18-8 Stainless Steel (AISI 304)

Other uses are as superconductive materials of TiNb, the shape memory alloy of Ti–Ni, the hydrogen occlusion alloy of Ti–Fe, and in computer equipment as nonmagnetic substance, artificial bones, dental roots, cardiac valves and cardiac pacemakers as nontoxic and biocompatible materials [3,5].

Titanium-sponge (purity: 99.2 % or more) is a spongy titanium. The total production capacity in Japan (30×10^3 tons), United States (28×10^3 tons), England (5×10^3 tons) and Soviet Union (48×10^3 tons) is about 110×10^3 tons worldwide, so it is a small amount compared with the production of aluminum (18 million tons).

The price of titanium-sponge is 1200–1400 yen/kg, and cast titanium (pure titanium) costs about 5000 yen/kg; hence they are relatively expensive. Titanium is expected to be used in sports goods and in marine development materials, since it has a high tensile strength and high corrosion resistance.

The main uses, apart from the metal itself, is as TiO_2, the production capacity of which is about three million tons, about thirty times larger than that of the metal. TiO_2 is a white pigment. It is used in paints, inks, synthetic resins, papers, synthetic fibers and rubbers. The particle size of titanium oxide is usually 0.2–0.3 μm. However, as super fine particles of 0.0015 μm–0.05 μm it has a transparency as well as UV absorption and this fine-particle titanium is widely used in cosmetics. Titanium oxide coated with a tin oxide doped antimony (SnO_2–Sb) is called conducive titanium, and is used as a conductive material and antistatic agent. Titanium black (TiO) produced by reduction of TiO_2 is used as a cosmetic black pigment (eyebrow pencil) and a conductive filler [7–10a]. $TiCl_3$ and $TiCl_4$ are used as

Ziegler-Natta catalysts. As barium titanate has high dielectric properties and piezoelectric properties, it is used for these properties, and in supersonic generators. Titanium tetraalkylester ($Ti(OR)_4$, R = *i*-Pr, Bu, etc.) is used as a repellent coating for fibers [8]. Since TiC and TiN have high melting points of about 3000 °C, and high degrees of hardness, they are used a high temperature resistant materials such as cutting tools and diesel engine valves of cermet [9,10].

12.3 PREPARATION OF ORGANOTITANIUM COMPOUNDS

Organotitanium compounds are prepared by reaction of titanium halides with organometallic compounds such as organoalkali metal compounds, Grignard reagents or organozinc compounds [11,12]. For example, tetramethyltitanium is prepared as follows [12]: tetrachlorotitanium is slowly mixed with methylmagnesium chloride at −78 °C, heated slowly to become homogenous, and the solution was allowed to stand overnight at −78 °C. A dark green solid is precipitated on the bottom of the reaction vessel. The supernant solution is removed and an ether/hexane solution is added to the residue and concentrated at −40 °C. Then the solution is left standing at −78 °C to form yellow crystals of tetramethyltitanium. The tetramethyltitanium is sensitive to oxygen and moisture, and decomposes at about −60 °C [13].

$$TiX_m \quad + \quad RM \longrightarrow R_nTiX_{4\text{-}n} \qquad (12.5)$$

M = Li, Na, MgX, 1/2 Zn
X = Cl, Br
R = alkyl

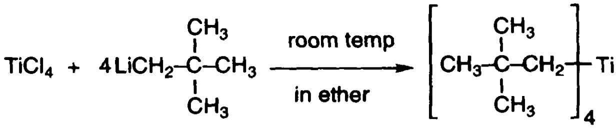
$$TiCl_4 \quad + \quad 4MeMgCl \xrightarrow[\text{in hexane}]{-78\ ^\circ C} Me_4Ti \qquad (12.6)$$

Pyridine is added to the ether solution of tetramethyltitanium to precipitate the solid substance. It is dissolved by adding a small amount of pentane at −30 °C, and then cooled at −78 °C to precipitate $Me_4Ti{\cdot}2py$ as a yellow crystal. The adduct is decomposed at 0 °C [14]. The decomposition temperatures of the other tetramethyltitanium adducts are as follows:

1,4-Dioxane adduct (yellow needles)	*ca.* −20 °C
Triethylamine adduct (yellow crystal)	0 °C or below
Trimethylphosphine adduct (yellow crystal)	0 °C or below
Bis(trimethylphosphine) adduct (orange needles)	*ca.* 20 °C
2,2′-Bipyridyl adduct (red crystals)	*ca.* 30 °C

All of the adducts are more stable than Me_4Ti [12,14,15].

Tetrakisneopentyltitanium is prepared as shown in eq. (12.7). Neopentyllithium reacts with titanium tetrachloride in ether solution at room temperature and the solvent is removed under reduced pressure. The remaining solid is dissolved in petroleum ether, and cooled at −20 °C to yield the crude product (60–80 % yield). The yellow crystalline product (30 % yield) is obtained by recrystallization [16].



$$\mathrm{TiCl_4} + 4\,\mathrm{LiCH_2}\text{–}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{–}\mathrm{CH_3} \xrightarrow[\text{in ether}]{\text{room temp}} \left[\mathrm{CH_3}\text{–}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{–}\mathrm{CH_2}\right]_4\!\text{–}\mathrm{Ti} \qquad (12.7)$$

The other alkyltitaniums tend to suffer β-elimination and generally are very liable. Tetraphenyltitanium, for example, as yellow crystals is prepared by mixing phenyllithium and titanium tetrachloride at −70 °C as shown in eq. (12.8) [17].

$$\mathrm{TiCl_4} \quad + \quad 4\mathrm{PhLi} \xrightarrow[\text{in ether}]{-70\ ^\circ\mathrm{C},\ 2\ \mathrm{hr}} \mathrm{Ph_4Ti} \qquad (12.8)$$

Tetraphenyltitanium starts to decompose at −20 °C and at room temperature it decomposes to diphenyltitanium and biphenyl [12,17].

$$\mathrm{Ph_4Ti} \xrightarrow{\text{room temp}} \mathrm{Ph_2Ti} + \mathrm{Ph\text{-}Ph} \qquad (12.9)$$

The cyclopentadienyltitanium compound is very stable compared with alkyltitanium or aryltitanium. For example, dicyclopentadienyltitanium halides melt at about 300 °C (Cp_2TiX_2, X = Cl 280 °C, X = Br 314 °C, X = I 319 °C). Hence, Cp_2TiX_2 is widely used as the starting material for organotitanium compounds. Cp_2TiCl_2 is prepared by the reaction of cyclopentadienyl compounds of Grignard reagents [18,19], sodium [18], lithium [20,21] or lead [22]. In the Russian patent, Cp_2TiCl_2 is prepared by the reaction of cyclopentadiene with $TiCl_4$ in the presence of diethylamine as shown in eq. (12.11) [11,23].

$$\mathrm{TiCl_4} \quad + \quad 2\mathrm{CpM} \longrightarrow \mathrm{Cp_2TiX_2} \qquad (12.10)$$

M = MgCl, MgBr, Na, Li, 1/2 Pb
X = Cl, Br

$$\mathrm{TiCl_4} \quad + \quad 4\mathrm{CpH} \xrightarrow[\text{in dioxane}]{60\text{ - }80\ ^\circ\mathrm{C},\ \mathrm{NHEt_2}} \mathrm{Cp_2TiCl_2} \qquad (12.11)$$

Cyclopentadienylaryl or cyclopentadienylalkyl derivatives of cyclopentadienyltitanium obtained by the reaction of cyclopentadienyltitanium with aryl metal compounds or alkyl metal compounds, are also stable by the stabilization action of the cyclopentadienyl ring. For example, Cp_2TiCl_2 reacts with phenyllithium to give the diphenyl derivatives. This compound decomposes at 105 °C to yield benzene [21].

$$Cp_2TiCl_2 \quad + \quad 2PhLi \xrightarrow{\qquad\qquad} Cp_2TiPh_2 \quad (12.12)$$

As shown in eq. (12.12a), the reaction with Me_3GeCH_2Li, give an orange colored crystalline cyclopentadienyl derivative, which melts at 136–138 °C, and decomposition starts at the melting point [24].

$$Cp_2TiCl_2 + 2Me_3GeCH_2Li \xrightarrow[\text{in ether}]{\text{room temp.}} Cp_2Ti(CH_2GeMe_3)_2 \quad (12.12a)$$

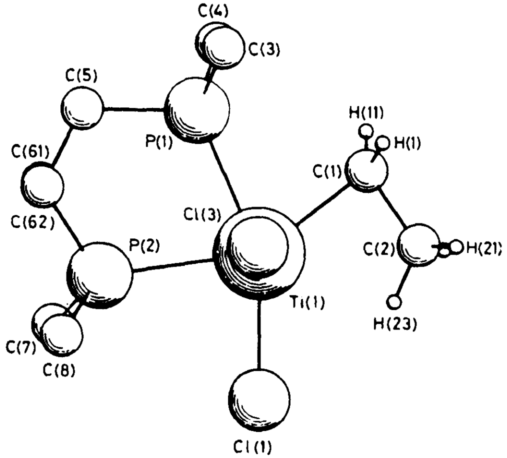
The corresponding silicon compound ($Cp_2Ti(CH_2SiMe_3)_2$) of the above compound is more stable, and it decomposes at 300 °C [24].

12.4 PROPERTIES OF ORGANOTITANIUM COMPOUNDS

Organotitanium compounds are less stable than the main group organometallic compounds of group 14 elements of Si, Ge, Sn and Pb and group 13 elements such as Al [25]. Transition elements are elements having an unoccupied d orbital. Titanium is one of the transition elements. The outer orbital electron configurations of titanium is $3s^23p^63d^24s^2$. That of tetraalkyltitanium is $3s^23p^63d^64s^2$. If the d orbital of titanium is completely occupied ($3s^23p^63d^{10}4s^2$), then it is stable. In tetraalkyltitanium the orbital of titanium is not completely occupied; then it forms hybrid orbital of 3d and 4s orbitals. However, in tetramethyltitanium described above, the adduct of electrondonating pyridine or amines, especially a four electron adduct, is stable because these four electron adducts form a $3d^{10}$ occupied 3d orbital [11].

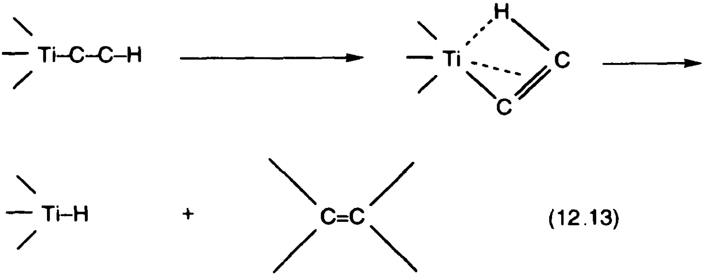
The other reason that the organotitanium compounds are not stable is, in particular, because alkyltitaniums are liable and its β-elimination tends to proceed. For example, titanium compounds having an ethyl group form a four electron adduct $Ti(Me_2PCH_2CH_2PMe_2)(EtCl_3)$ as shown in Figure 12.1 [26].

The crystal structure of carbon is usually tetrahedral and the bond angle is 109°28′. However the bond angle in Ti-C(1)-C(2) is small, 85.89°. In contrast, that of C(1)-C(2)-H(23) is very large, 124.41°, and the bond angle of C(2)-H(23)-Ti is 90.4°. Thus, the hydrogen (H(23)) bonded with β-carbon is at the position where it rather bonds with Ti. Therefore, both Ti-C(1)-C(2) and C(1)-C(2)-H(23) are in a very strained state and the bond distance of Ti-H(23) is 2.29 Å. The sum of covalent



Figured 12.1 Crystal structure of [Ti($Me_2PCH_2CH_2PMe_2$)$EtCl_3$] showing the plane containing the P_2TiC_2H (23) atom [26].

radii and the sum of van der Waals radii of Ti and H are estimated to be 1.75 Å and 3.32 Å, respectively [27–29]. The value of 2.29 Å is nearer to the sum of covalent radii than the sum of van der Waals radii. It is considered that a Ti-H(23) bond forms a bond resembling a covalent one. On the other hand, the length of the Ti-C(1) bond is 2.154 Å and that of a Ti-C(2) bond is 2.516 Å. The difference in these two bonds is very small, and the bond length of C(1) and C(2) is 1.463 Å, i.e. near the value of the double bond. Therefore, the bond of C(1) and C(2) is thought to form a π-coordination bond to Ti as shown in eq. (12.13).



(12.13)

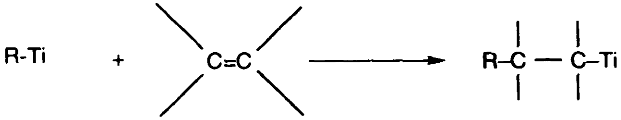
That is the reason that hydrogen at the β-position is liable to be eliminated, i.e. the hydrogen forms a quasi covalent bond between the hydrogen (β-hydrogen) and metal, the carbon–carbon bond (-C(1)-C(2)-) is close to the carbon–carbon double bond and forms a weak π-bond to metal. Therefore, metal-C(1)-C(2)-H forms a distorted four-membered ring structure. Hence, these bonds are easily decomposed.

The Ti-H-C(2) is a three-center two-electron bond, i.e. an electron deficient bond. This bond is an agostic bond (agostic is derived from Greek: 'grasp to oneself', and it is a bond between the σ-electron of C—H bond and the vacant d-orbital of the metal [29a].

Therefore, methyltitanium compounds and neopentyltitanium compounds not having a β-carbon atom are relatively stable as alkyltitanium compounds. The phenyl and other aryl titanium compounds are relatively stable. As described above, titanium compounds having cyclopentadienyl groups are stable and have a high melting point. Cp_2TiCl_2 forms a π-coordination distorted tetrahedral structure [30].

Recently, titanocene compounds such as Cp_2TiCl_2 [30a,30b], titanium compounds coordinated with similar cyclopentadienyl ring [30m–30o] and tetrahedral organotitanium compounds [30p–31] have been reported.

With organotitanium compounds, especially carbometalation, substitution and insertion reactions tend to proceed. Carbometalation, as described in the reaction mechanisms of the Ziegler–Natta catalyst in Chapter 7, contains olefin polymerization with titanium compounds. Namely, titanium reacts with organoaluminum compounds and the titanium atom forms a bridged structure (Ti—R—Al) with an alkyl group of organoaluminum compounds and this Ti—R adds to a carbon–carbon double bond.



(12.14)

The substitution reaction, for example, is the synthetic reaction of amino compounds as shown in eq. (12.15) [32].

$$Cp_2TiCl_2 + 2LiNMe_2 \longrightarrow Cp_2Ti(NMe_2)_2 \quad (12.15)$$

The insertion reaction of alkyl group tends to proceed. For example, carbon monoxide is easily inserted into the Ti—R bond as shown in eq. (12.16) [33,33a].

$$XCp_2TiR + CO \longrightarrow Cp_2TiCOR(X) \quad (12.16)$$

$R = Me, Et, CH_2Ph$
$X = Cl, I, CH_2Ph$

Tetravalent titanium compounds are easily reduced to trivalent titanium compounds with metals such as sodium, magnesium and zinc. Trivalent, such as Cp_2TiCl, and lower valence organotitanium compounds are easily oxidized, i.e.

$$Cp_2TiCl_2 + 1/2\,Zn \longrightarrow Cp_2TiCl + 1/2\,ZnCl_2 \quad (12.17)$$

they have a strong reductive power. Therefore, they are used for organosynthetic reactions. Lower valence organotitanium compounds have trivalence, divalence and zero valence [34]. For example:

Ti(III) Cp_2TiCl, $CpTiCl_2$
Ti(II) $CpPhTi(OEt_2)_2$, $Cp_2T(PMe_2Ph)_2$
Ti(0) $(\eta^6\text{-}C_6H_6)_2Ti$

12.5 APPLICATIONS OF ORGANOTITANIUM COMPOUNDS

12.5.1 ORGANOTITANIUM COMPOUNDS

Organotitanium compounds are usually liable besides cyclopentadienyltitanium compounds. Therefore, titanium organic compounds are not organotitanium compounds having a Ti–C bond but titanium alkoxide having a Ti–O bond [11,35].

Titanium alkoxides are described first since they are widely used. The titanium alkoxides ($Ti(OR)_4$) are synthesized by the reaction of titanium tetrachloride with alcohol in the presence of ammonia or amines. The tetrabutoxide of the representative alkoxide is a liquid compound, with a boiling point of 134–136 °C/1 mmHg. Titanium alkoxide absorbs moisture from air, is hydrolyzed, forms –Ti–O–Ti–O–, and forms a transparent film. Therefore, $Ti(O\text{-}i\text{-}Pr)_4$ is used as a surface treatment for the prevention of damage and scratching of glass. $Ti(OBu)_4$ is used as additives in heat-resistant paint (up to 500–600 °C) [11].

$$TiCl_4 + 4ROH \xrightarrow{4NH_3} Ti(OR)_4 + 4NH_4Cl \qquad (12.18)$$

As the Ti of titanium alkoxides shows a strong affinity to oxygen, they are able to bond to the oxygen in polymers (for example, polyesters, polyamides, polyimides, epoxides, acrylic resins and celluloses), metal oxides, nonmetal oxides, and oxygen-containing group (e.g., OH) on the surface of a metal. Hence, they are used as adhesives, catalysts for esterification or ester exchange reaction, catalysts for epoxide resins, activators of peroxides, pigment stabilizers of paint, sand floating agent and paper sizing agents, etc. [11].

The usages of organotitanium compounds are the following four items:

(1) Thin film forming materials
(2) Anticancer drugs
(3) Catalysts for polymers
(4) Organosynthetic agents

Organotitanium compounds for these usages are mainly cyclopentadienyl compounds. The others are Ti-Ph, $Ti\text{-}CH_3$ and $Ti\text{-}CH_2C(Me)_3$, etc.

12.5.2 THIN FILM FORMING MATERIALS

The usual techniques of vacuum vaporization, wet electroplating and electroless plating are difficult to use to form a homogenous pinholeless metal thin film. Recently MOCVD process (Metal Organic Chemical Vapor Deposition Process), which is able to resolve these problems, has attracted public attention. The most characteristic organometallic compounds are easily available as very high purity single metallic materials for thin film forming materials.

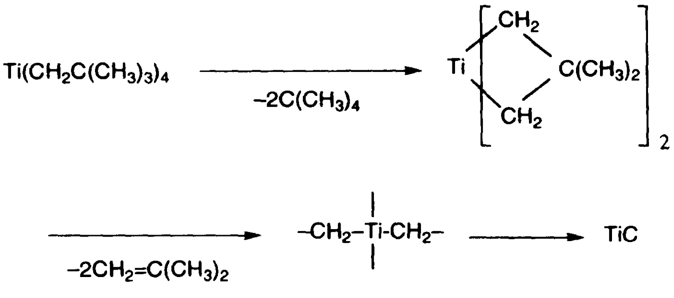
Organotitanium compounds are used as the raw materials for metal carbides. Titanium carbide (TiC), for which the Mohs hardness is close to that of diamond, 9–10, has a high heat resistance (mp $3067\,^{\circ}\mathrm{C}$) and resistant to acid or alkali [36]. Hence, TiC is useful as abrasion resistant coating materials such as the lining of fusion reaction vessel, cutting tools and bearings, etc. The CVD process (Chemical Vapor Deposition Process) of a TiC coating is carried out by heating $TiCl_4$, H_2 and CH_4 at $1000\,^{\circ}\mathrm{C}$.

Recently, William and co-workers [36] have produced a TiC coating with the product obtained from the reaction of the reactive titanium ethoxide with organolithium compounds as shown in eq. (12.18a). The product is isolated as yellow

$$\mathrm{Ti(OCH_2CH_3)_4} + \mathrm{4LiCH_2C(CH_3)_3} \longrightarrow \mathrm{Ti(CH_2C(CH_3)_3)_4} \qquad (12.18a)$$

crystalline tetraneopentyltitanate by sublimation at $50\,^{\circ}\mathrm{C}/10^{-3}$ mmHg, and evaporates at *ca.* $150\,^{\circ}\mathrm{C}/10^{-5}$ mmHg. This MOCVD process is able to evaporate the *ca.* 2 μm layer over six hours with 1 g of titanium compounds. This process is able to form a thin film having the same hardness at low temperatures compared with the film produced by the usual process. The thin film forming reaction is considered as shown in Scheme 12.1 [36]; elimination of a neopentyl group is accompanied by the elimination of hydrogen at the γ-position to form titanium cyclobutane, and isobutylene is eliminated to form $-(CH_2)-Ti-(CH_2-)$ and it further decomposes to TiC [36].

$Ti(BH_4)_3$ (dme) (dme: 1,2-dimethoxyethane, $CH_3-OCH_2CH_2-OCH_3$) is not an organometallic compound, it gives TiB_2 by heating at $200\,^{\circ}\mathrm{C}/10^{-4}$ mmHg. TiB_2



Scheme 12.1

(mp 2900 °C) is used in aircraft material since it has a high hardness and high heat resistance [37,38].

12.5.3 ANTICANCER DRUGS

Organotitanium compounds were first tested as anticancer drugs in 1979. Ehrlich ascites tumor cells were implanted in 84 mice by intraperitoneal injection. 24 hours after transplantation, these mice were treated (likewise intraperitoneally) with Cp_2TiCl_2 in doses varying between 10 and 140 mg/kg. All untreated control (0.4 ml DMSO–NaCl solution, 12 mice) died as a result of tumor growth within 30 days. As shown in Figure 12.2, the mice with doses of 30–80 mg/kg of Cp_2TiCl_2 survived with a cure rate in the therapeutic range of over 80 %. The survival rate of those with doses of more than 80 mg/kg decreased due to side effects [39].

Cp_2TiCl_2 is also used for treatments of lymphoid leukemia L1210, P388 and ILS (the value of the increase in the life span) is 125 % or more compared with the untreated control [40].

Recently, the studies of $Cp_2Ti(OCOR)_2$ ($R=H$, Me) on lymphoid leukemia L1210, show that they have a slightly lower value than Cp_2TiCl_2 [41].

The anticancer effect of organotitanium compounds is lower than those of cisplatin of platinum and organotin compounds [42], at this stage, they are not used for remedy yet.

12.5.4 POLYMERIZATION CATALYSTS

Cyclopentadienyltitanium compounds have been studied as polymerization catalysts of ethylene as Ziegler–Natta type catalysts [43–45a]. For example, as

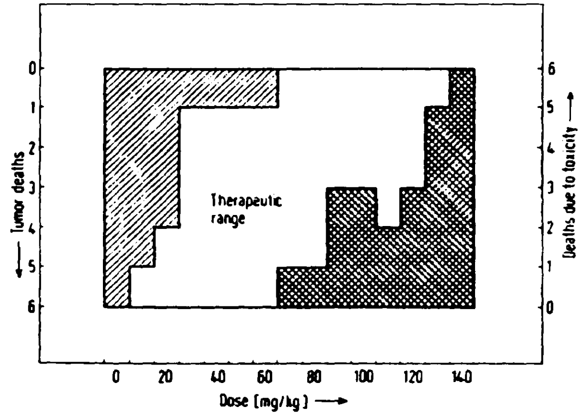


Figure 12.2 Survival of mice 30 days after tumor transplantation and 29 days after treatment with Cp_2TiCl_2 at the doses given on the abscissa [39]. ▨, tumor deaths without signs of substance toxicity. ▩, Deaths caused by toxicity (deaths after 8 days after transplantation without macroscopically visible tumor development). ☐, Animals surviving on the 30th day after transplantation (therapeutic range)

described in Chapter 7 [31], for Cp_2TiCl_2-$AlEt_3$ it is thought that the polymerization proceeds with the same reaction mechanism as $TiCl_3$-$AlEt_3$ [43].

The reaction rate with $Cp_2TiEtCl/AlEtCl_2$, is faster than that with $Cp_2TiCl_2/AlEtCl_2$ or $Cp_2TiCl_2/AlEt_2Cl$, it is 15 $dm^3\ mol^{-1}\ s^{-1}$ at 10 °C [46]. However, as reviews of Ishioka [47] and Kashiwa [48–51] show, the titanium component of Ziegler–Natta type catalysts show only $TiCl_3$ and $TiCl_4$. Therefore it is a problem whether organotitanium compounds are used industrially.

Recently, many titanium compounds have been studied as polymerization catalysts of olefins [51a–51f]. In these studies, the active center of ethylene polymerization with Ziegler–Natta type catalysts by using a square-pyramidal model is thought to be a weak π-bond between ethylene and titanium. The bond length and bond energy are calculated 2.80 Å and 7–11 kcal/mole, respectively [51a].

12.5.5 ORGANOSYNTHETIC REAGENTS

Recently, many reviews of organotitanium compounds on reagents for organosynthetic reaction have been reported, especially on low valent titanium compounds [34,52–61].

Organotitanium compounds have a strong affinity to oxygen and tend to become TiO_2. The low valence titanium compounds show a stronger reductivity since they are liable to be more oxidized than tetravalent titanium compounds. Low valence titanium compounds are not only trivalent or less, but also tetravalent compounds which yield the low valence compounds in the reaction system. If the tetravalent titanium compounds react in the presence of reducing agents such as metals or metal compounds, they are reduced to Ti(III), Ti(II), Ti(I) and Ti(0).

In titanium compounds and reducing agents, as the titanium compounds are inorganic compounds, Mukaiyama [62,63] reported $TiCl_4/Zn$ and $TiCl_4/LiAlH_4$ in 1973, McMurray and co-workers [64] reported $TiCl_3/LiAlH_4$ in 1974. The other is $TiCl_3/Li$, $TiCl_3/K$, $TiCl_3/Mg$, $TiCl_4/BuLi$, etc. [54]. In these reagents, $TiCl_3/LiAlH_4$ is widely used and it is called the McMurry reagent [54]. The reductive coupling reaction used this reagent is called the McMurry reaction [55].

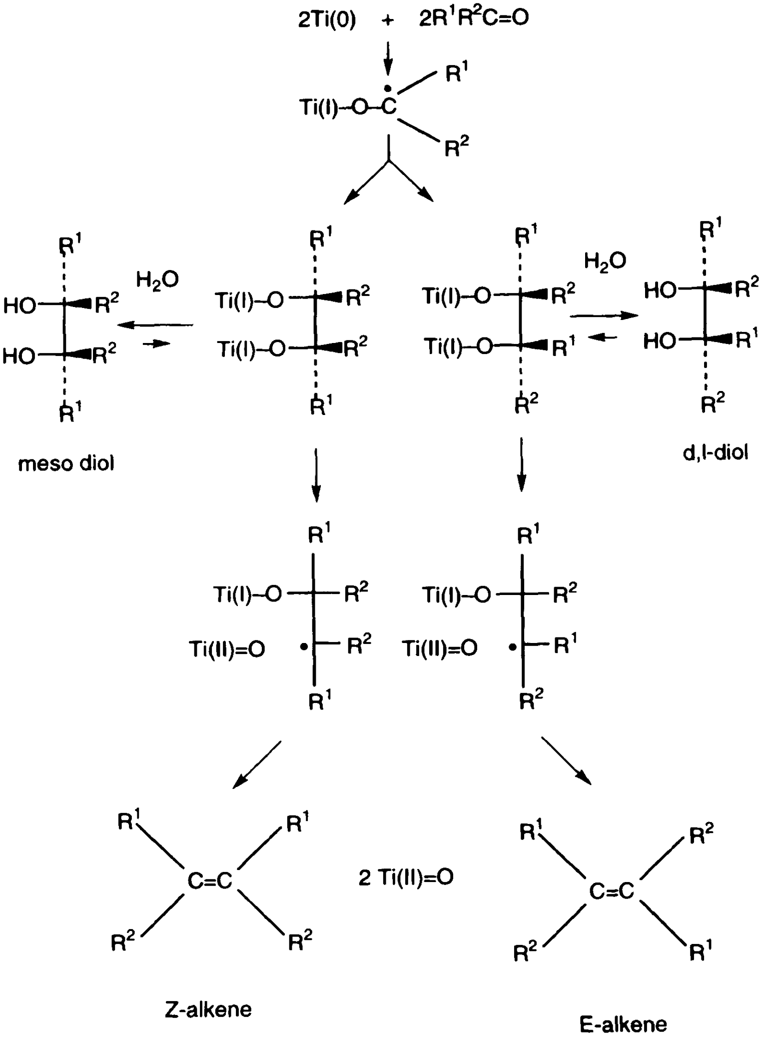
Tetravalent organotitanium compounds and reducing agents as the reagents of low valence organotitanium compounds are Cp_2TiCl_2/M (M = Zn, Na, Mg, Al, Na/Hg, etc.). These reaction systems yield, e.g., $[Cp_2Ti(III)\ Cl]_2$. Ti(II) is $Cp_2Ti(PF_3)_2$ and $Cp_2Ti(CO)_2$, etc. Ti(0) is $(\eta^6$-$C_6H_6)_2Ti$, etc. [57].

The representative reactions with low valence organotitanium reagents are the following two reactions.

(1) Reductive coupling
(2) Elimination

Reductive coupling is that, for example, aldehydes or ketones are reduced at 0 °C or below, and diols are prepared by coupling reactions. Further heating yields alkenes [56]. Dames and co-worker [65] found with ESR that Ti(III) in the reaction system with McMurry reagents or $TiCl_3/M$ (M = Li, K, Mg), is reduced to Ti(I) or Ti(0).

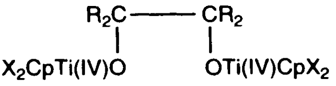
Ketone reacts with $TiCl_3/M$ (M = Li, K, Mg) as shown in Scheme 12.2 [55] and in the first stage, electron transfers from Ti to the carbonyl group yield the radical anion. Then the ketyl radical dimerizes to the corresponding pinacol, which can be isolated as the primary reaction product of low temperatures. Deoxygenation by a cis-type concerted mechanism of the pinacol occurs readily, leading to alkenes, due to the large affinity of titanium for oxygen. The ratio of the diol formation of meso,



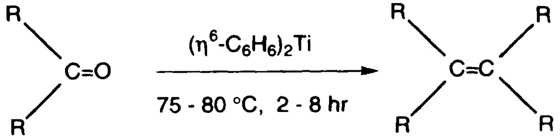
Scheme 12.2 [55].

d,l-isomers and the ratio of the olefin formation of E/Z-isomers depends strongly on the choice of titanium reagent and steric bulk of the alkyl groups [55].

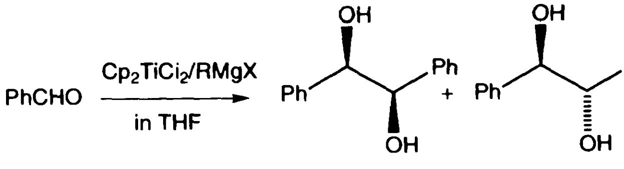
Generally, the reducing power of low valence organotitanium compounds is smaller compared to inorganic reagents such as a McMurray reagent. Therefore the reaction of ketones with $CpTiCl_3/LiAlH_4$, or Cp_2TiCl_2/M (M = Zn, Mg, RMgX) only yields pinacol [57]. For example, the reaction of acetone or benzophenone with $CpTi(III)X_2$ (X = Cl, Br) yields a yellow or green pinacol complex [66]. But divalent $Cp_2Ti(CO)_2$ and zero valent $(\eta^6\text{-}C_6T_6)_2Ti$ are reactive, so their reactions yield alkenes [57]. In particular, the zero valent $(\eta^6\text{-}C_6H_6)_2Ti$ is reactive and the reactions of acetone or benzophenone yield alkenes quantitatively [67]. On the other hand, the reducing power of tetravalent or trivalent organotitanium compounds are weak. As they have various organic groups, they are able to let the highly stereoselective reaction proceed as shown in eq. (12.20) [68,69].



R = Me, Ph
X = Cl, Br



(12.19)



(12.20)

threo 80 : 1 erthro

Elimination is the reaction that shows a strong affinity of titanium to oxygen. Highly reactive $(\eta^6\text{-}C_6H_6)_2Ti$ is able to yield diphenylacetylene by elimination of two oxygen atoms of benzil (PhCOCOPh) [67]. However, the reaction of $PhCOCH_2COPh$ with $Cp_2TiCl_2/LiAlH_4$ gives $PhCH_2CH_2COPh$ in yield of 90 % or more the reduction of only one carbonyl group [57].

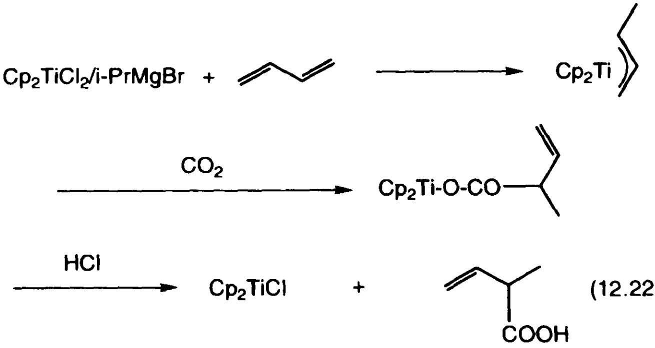
$$\mathrm{PhCOCOPh} \xrightarrow[80\ °\mathrm{C},\ 2\ \mathrm{h}]{(\eta^6\text{-}C_6H_6)_2Ti} \mathrm{PhC{\equiv}CPh} \qquad (12.21)$$

96 %

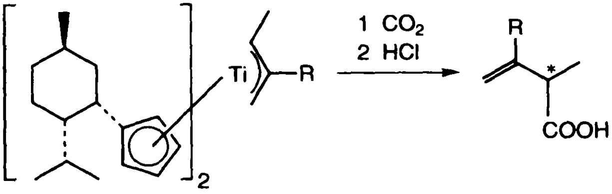
In the other reactions with Cp_2TiCl, $Cp_2TiCl_2/LiAlH_4$ or $CpTi(CO)_2$, the elimination of oxygen from epoxides gives alkenes, and elimination of oxygen from sulfoxide give a thioether [57]. As a reduction with low valence titanium compounds, for example, cis-olefin is prepared from disubstituted acetylene [57].

The other reactions with low valence organotitanium compounds are the fixation of nitrogen, or the reaction with small molecules such as CO_2, $CH{\equiv}CH$ and CO [57]. A metal which is able to fix nitrogen by reaction with a nitrogen atom is Mo, Co, Zr, W and Mn [29a]. Titanium compounds are also able to form the complex with nitrogen, and nitrogen-containing compounds are isolated by reaction with reactive compounds such as acid halides [70]. For example, $Cp_2Ti(PMe_3)_3$ reacts with nitrogen to yield $[Cp_2Ti(PMe_3)_2]_2(\mu\text{-}N_2)$ [71].

CO_2, as a small molecule, is inserted into $Cp_2Ti(\pi\text{-allyl})$ and the carboxylic aid is isolated by adding hydrochloric acid as shown in eq. (12.22). In the synthetic reaction of carboxylic acid, as shown in eq. (12.23), with chiral cyclopentadienyl titanium compounds having an asymmetric carbon bonded to the cyclopentadienyl ring, the optically active carboxylic acid yields [72].



(12.22)



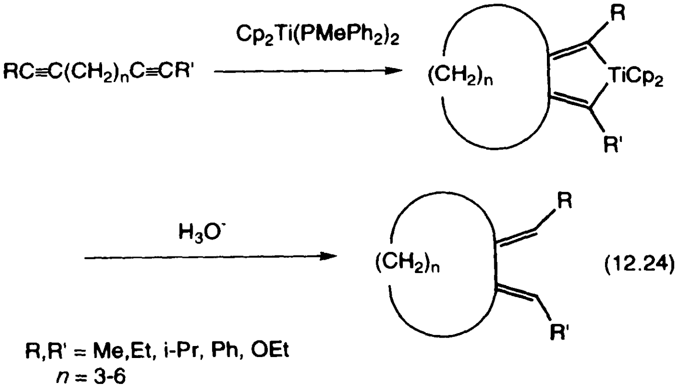
(12.23)

R = H [α]$^{25}_{D}$ +7.23°

R = Me [α]$^{25}_{D}$ -7.32°

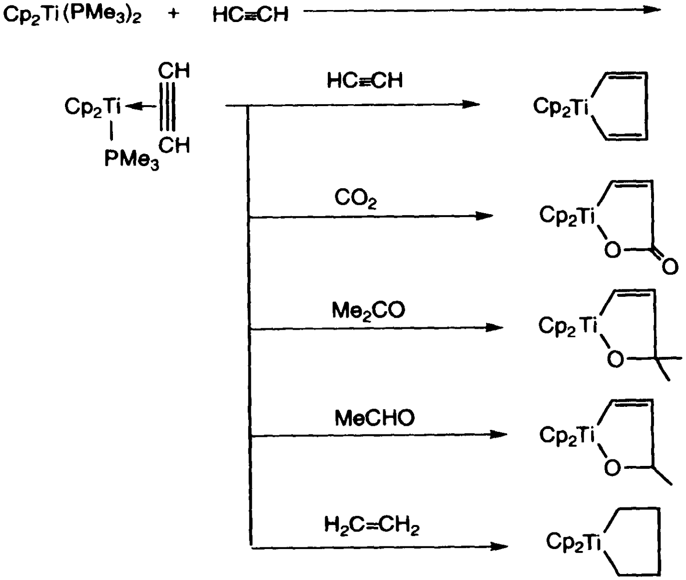
$Cp_2Ti(PMe_3)_2$ reacts with acetylene to form the acetylene π-complex. Furthermore, the complex reacts with acetylene, CO_2, acetone, acetaldehyde, ethylene, etc.

to form the five-membered ring compounds having titanium [72,73]. These five-membered rings are easily opened by hydrolysis to yield the hydrolyzates. Scheme 12.3 [74] shows two-step reactions of the formation of cyclotitanium compounds. However, the reactions with diacetylene compounds yield a cyclotitanium compound by a one-step reaction, and the ring-opening reaction product is obtained by hydrolysis as shown in eq. (12.24) [53,74a].



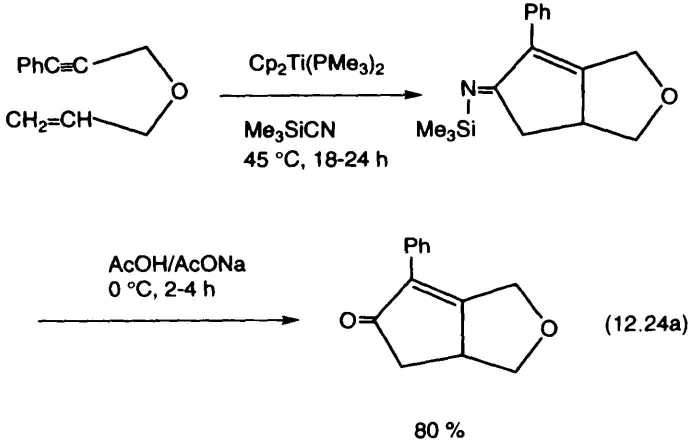
R,R' = Me,Et, i-Pr, Ph, OEt
$n = 3\text{-}6$

(12.24)



Scheme 12.3 [74]

As shown in Scheme 12.3 and eq. (12.24), acetylenic compounds cyclize with titanocenes to yield the metalacylo compounds. This cyclization with cyano compounds gives the imino compounds as shown in eq. (12.24a). This reaction is considered to proceed via the titanocyclo compounds shown in eq. (12.24). The imino compound is added to organic acids to give the ketone as shown in eq. (12.24a) [74b].

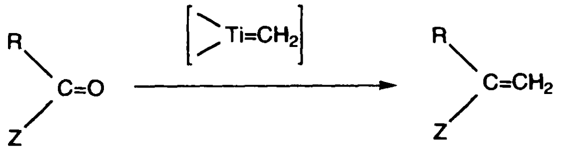


(12.24a)

As reactions with tetravalent organotitanium compounds, the following four reactions are particularly noted.

(1) Carbonyl methylenation
(2) *Gem*-dimethylation
(3) Selective addition to carbonyl groups
(4) Stereospecific reaction

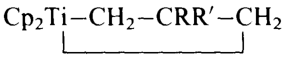
Carbonyl methylenation is the reaction when the carbonyl group changes to a vinyl group as shown in eq. (12.25). Hence, as it is the same as the methylenation of Wittig reaction, it is called Wittig methylenation [75]. In carbonyl methylenation, the reagent which yields a carbene complex (Ti$=$CH$_2$) in the reaction system is



(12.25)

$Z = H, R', OR', NR_2', NR'COR''$

used. For example, $Cp_2TiCl_2/AlMe_3$ (Tebbe reagent [75,76]), metalacyclobutane compound, e.g. the reaction product of the Tebbe reagent with olefins,

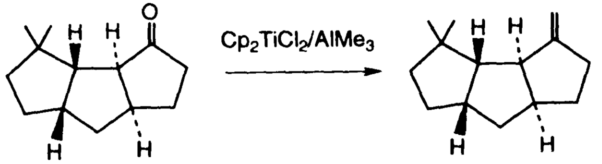


$$Cp_2Ti{-}CH_2{-}CRR'{-}CH_2$$

($R,R' = H$, *t*-Bu, *i*-Pr) [77], and $TiCl_4/Zn/CH_2Br_2$ [78].

Carbonyl methylenation proceeds with not only a ketone, like the Wittig reaction, but also with carbonyl-containing compounds such as aldehydes, esters and amides as shown in eq. (12.25). Therefore, carbonyl methylenation is a more widely applicable reaction than the Wittig reaction.

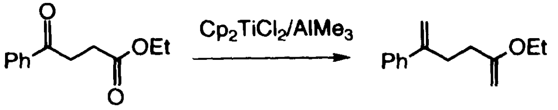
As methylenation of ketone, for example, the synthesis reaction of capnellene or the capnellane precursor of sesquiterpene is shown in eq. (12.26) [75,79].



capnellene

(12.26)

Organotitanium compounds are able to react with compounds having both keto carbonyl groups and ester carbonyl groups, and they are able to change these two groups to two methylene groups, different from the Wiggit reagent, as shown in eq. (12.27) [80].

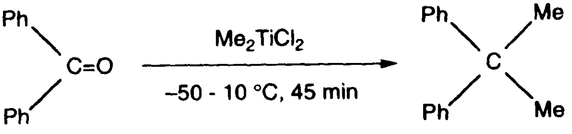


(12.27)

In alkyltitanium compounds, the reactivity increases if the number of alkyl group increases. The order of the reactivity is as follows [58]:

$$MeTi(OR)_3 < Me_2Ti(OR)_2 < Me_3TiOR < Me_4Ti$$

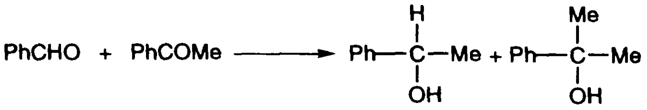
For example, Me_2TiCl_2 is more reactive than $MeTiCl_3$. With Me_2TiCl_2, *gem*-dimethylenation of ketocarbonyl proceeds [81]. For example, the reaction of diphenylketone is shown in eq. (12.28). Reaction selectivity of Grignard reagents



(12.28)

83 %

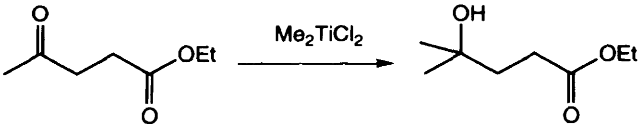
and organolithium compounds to the carbonyl group is low. But the reactivities of organotitanium compounds to aldehydes and ketones, or to ketones and esters, are very different. This high reaction selectivity of organotitanium compounds is thought to result from the fact that the reactivity of organotitanium compounds is low compared to Grignard reagents and organolithium compounds, and that the polarity of Ti-C is low [58]. For example, if MeLi reacts with the mixture of benzaldehyde and acetophenone, and the reaction products are hydrolyzed, then these two compounds are almost equally methylated, but in the reaction with $MeTi(OCHMe_2)_3$ most of the aldehyde is selectively methylated as shown in eq. (12.29) [82].



$$\mathrm{PhCHO + PhCOMe \longrightarrow Ph{-}\overset{H}{\underset{OH}{C}}{-}Me + Ph{-}\overset{Me}{\underset{OH}{C}}{-}Me} \qquad (12.29)$$

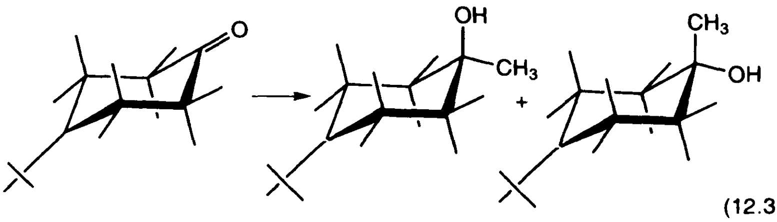
MeLi	2	:	3
$MeTi(OCHMe_2)_3$	>98	:	2

As shown in eq. (12.30), levulinic acid ethylester has two kinds of carbonyl: ketacarbonyl and estercarbonyl. Me_2TiCl_2 then selectively reacts with a keto-carbonyl group, and the methylated alcohol esters are prepared in 90% or more yield [83].



(12.30)

Organotitanium compounds show higher stereospecificity than Grignard reagents and organolithium compounds. For example, as shown in eq. (12.31) in the methylation of 4-*t*-butylcyclohexanone, both Grignard reagents and organolithium compounds selectively attack from the equatorial side which has less steric hindrance. This tendency with dimethyltitanium is much marked, and with more bulky monomethyltitanium this tendency is much more marked as shown in eq. (12.31) [58,83].

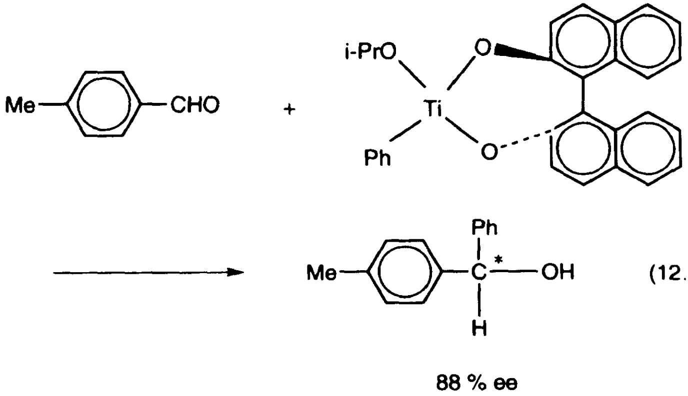


(12.31)

MeMgI	62	:	38
MeLi	65	:	35
Me_2TiCl_2	82	:	18
$MeTi(OCHMe_2)_3$	94	:	6

Organotitanium compounds having an optical active functional group react with an aldehyde to produce an optically active alcohol in high enantioselectivities of up to 88 % ee as shown in eq. (12.32) [84].

Recently, many enantioselective reactions with chiral titanium compounds as shown in eq. (12.32) have been reported [85–90].



(12.32)

REFERENCES

[1] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.

[2] *Shinkinzoku Databook*, Kinzoku Jihyo Henshubu ed., Homatt Ado. 1990.

[3] *Titan no Sekai*, Japan Titanium Society, 1991.
T. Imai, *Kagaku Keizai*, April (1994) 45.

[4] *Kagaku Binran Oyohen*, Japan Chemical Society, p. 289, 1980.

[5] T. Yabe, *Gendai Kagaku*, April (1983) 56.

[5a] *Kagaku Bibran Kisohen*, Japan Chemical Society, p. 1, 1984.

[6] *Kagaku Daijiten*, Tokyo Kagaku Dojin, p. 1411, 1989.

[7] *Kagaku Kogyo Jiho*, July 15, 1990.

[8] *Technopia, Encyclopedia of Science and Technology (Sekai Kagaku Daijiten)* **11**, Kodansha, Tokyo, p. 422, 1977.

[9] K. Ohhashi and T. Ohtsuka, *Kogyo Rare Metal*, No. 77 (1982) 96.

[10] H. Suzuki, K. Hayashi and H. Matsubara, *Nippon Kinzoku Gakkai Kaiho*, **22** (4) (1983) 312.

[10a] T. Yashuhara, *Kagaku to Kogyo*, **69** (1995) 320.

[11] Kirk-Othmer, *Encylopedia of Chemical Technology*, 3rd ed., New York, vol. 23, p. 176, 1980.

[12] *Methoden der Organishen Chemie*, Houben-Weyl, Berlin, Band XIII/7, p. 262, 1975.

[13] H.J. Berthold and G. Groh. *Z. Anorg. Chem.*, **319** (1963) 230.

[14] K.H. Thiele, *Pure Appl. Chem.*, **30** (1972) 575.

[15] J. Müller and K.H. Thiele, *Z. Anorg. Chem.*, **362** (1968) 120.

[16] W. Mowat and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, (1963) 1120.

[17] V.N. Latjaeva, G.A. Razuvaev, A.V. Malisheva and G.A. Kiljakova, *J. Organomet. Chem.*, **2** (1964) 388.

[18] G. Wilkinson and J.M. Birmingham, *J. Am. Chem. Soc.*, **76** (1954) 4281.

[19] G. Wilkinson, P.L. Pauson, J.M. Birmingham and F.A. Cotton, *J. Am. Chem. Soc.*, **75** (1953) 1011.

[20] L. Summers, R.H. Uloth and A. Holmes, *J. Am. Chem. Soc.*,. **77** (1955) 3604.

[21] L. Summers and R.H. Uloth, *J. Am. Chem. Soc.*, **76** (1954) 2278.

[22] A.K. Holliday, P.H. Hakin, R.J. Puddephatt and J.D. Wilkins, *J. Organomet. Chem.*, **57** (1973) C45.

[23] *USSR Patent* 825, 534 (May 7, 1981), Y.A. Sorokin and co-workers.

[24] M.R. Collier, M.F. Lappert and R. Pearce, *J. Chem. Soc. Dalton Trans.*, (1973) 445.

[25] *Yukikinzoku no Kagaku to Ooyo*, Asakura Shoten, p. 92, 1962.

[26] Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa and Keith Prout, *J. Chem. Soc. Chem. Commun.*, (1982) 802.

[27] L. Paluling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1942.

[28] A. Bondi, *J. Phys. Chem.*, **68** (1964) 441.

[29] *Kagaku Binran Kisohen*, Japan Chemical Society, p. II-717, 1984.

[29a] H. Yamazaki and Y. Wakatsuki, *Yukikinzoku no Kagaku (Organometallic Chemistry)*, Japan Chemical Society ed. Dainippon Tosho, 1989.

[30] A. Clearfield, D.K. Warner, C.H. Saldarriaga-Molina and R. Ropal, *Can. J. Chem.*, **53** (1975) 1622.

[30a] J. Scholz, F. Rehbaum, K.-H. Thiele, R. Goddard, P. Betz and C. Krüger, *J. Organomet. Chem.*, **443** (1993) 93.

[30b] E. Samuel, J.L. Atwood and W.E. Hunter, *J. Organomet. Chem.*, **311** (1986) 325.

[30c] M. Bochmann, L.M. Wilson, M.B. Hursthouse and R.L. Short, *Organometallics*, **6** (1987) 2556.

[30d] R. Beckhaus, T. Wagner, C. Zimmermann and E. Herdtweck, *J. Organomet. Chem.*, **460** (1993) 181.

[30e] U. Thewalt and T. Wöhrle, *J. Organomet. Chem.*, **464** (1994) C17.

[30f] B.E. Burstern, M.R. Callstrom, C.A. Jolly, L.A. Paquette, M.R. Sivik, R.S. Tucker and C.A. Wartchow, *Organometallics*, **13** (1994) 127.

[30g] I. Jibril, S.T. Abu-Orabi, S.A. Klaib, L. Zsolnai and G. Huttner, *J. Organomet. Chem.*, **467** (1994) 189.

[30h] S.L. Borkowsky, N.C. Baenziger and R.F. Jordan, *Organometallics*, **12** (1993) 486.

[30i] J. Britten, Y. Mu, J.F. Harrod, J. Polowin, M.C. Baird and E. Samuel, *Organometallics*, **12** (1993) 2672.

[30j] S. Gutmann, P. Burger, H.-U. Hund, J. Hofmann and H.-H. Brintzinger, *J. Organomet. Chem.*, **369** (1989) 343.

[30k] K. Hortmann, J. Diebold and H.-H. Brintzinger, *J. Organomet. Chem.*, **445** (1993) 107.

[30l] S.C. Sutton, M.H. Nantz and S.R. Parkin, *Organometallics*, **12** (1993) 2248.

[30m] W. Röll, L. Zsolnai, G. Huttner and H.H. Brintzinger, *J. Organomet. Chem.*, **322** (1987) 65.

[30n] W.W. Ellis, T.K. Hollis, W. Odenkirk, J. Whelan, R. Ostrander, A.L. Rheingold and B. Bosnich, *Organometallics*, **12** (1993) 4391.

[30o] R.D. Rogers, M.R. Sivik and L.A. Paquette, *J. Organomet. Chem.*, **450** (1993) 125.

[30p] R.O. Duthaler, A. Hafner, P.L. Alsters, P. Rothe-Streit and G. Rihs, *Pure Appl. Chem.*, **64** (1992) 1897.

[30q] A. Martín, M. Mena, C. Yélamos, R. Serrano and P.R. Raithby, *J. Organomet. Chem.*, **467** (1994) 79.

[30r] E. Solari, C. Floriani, K. Schenk, A. Chiesi-Villa, C. Rizzoli, M. Rosi and A. Sgamellotti, *Inorg. Chem.*, **33** (1994) 2018.

[31] J.E. Ellis, D.W. Blackburn, P. Yuen and M. Jang, *J. Am. Chem. Soc.*, **115** (1993) 11616

[32] C.R. Bennett and D.C. Bradley, *J. Chem. Soc. Chem. Commun.*, (1974) 29.

[33] G. Fachinetti and C. Floriani, *J. Organomet. Chem.*, **71** (1974) C5.

[33a] G. Fachinetti and C. Floriani, *J. Chem. Soc. Chem. Commun.*, (1972) 654.

[34] M. Bottrill, P.D. Gavens and J. McKeeking, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.1, p. 281, 1982.

[35] I. Sugiyama, *Titanium and Zirconium (Japan)*, **21** (1973) 136.

[36] G.S. Girolami, J.A. Jensen, D.M. Pollina, W.S. Williams, A.E. Kaloyeros and C.M. Allocca, *J. Am. Chem. Soc.*, **109** (1987) 1579.

[37] H. Yasuda, *Shokubai*, **32**(3) (1990) 196.

[38] J.A. Jensen, J.E. Gozum, D.M. Pollina and G.S. Girolami, *J. Am. Chem. Soc.*, **110** (1988) 1643.

[39] H. Köpf and P. Köpf-Maier, *Angew. Chem. Int. Ed. Engl.*, **18** (1979) 477.

[40] P. Köpf-Maier, W. Wagner, B. Hesse and H. Köpf, *Europe. J. Cancer*, **17** (1981) 665.

[41] H. Yasuda, T. Yasuhara, H. Yamamoto, K. Takei and A. Nakamura, *Chem. Express*, **3** (1988) 375.

[42] I. Omae, *Kagaku Kogyo*, **41** (1990) 944.

[43] P.D. Gavens, M. Bottrill, J.W. Kelland and J. McKeeking, *Comprehensive Organometallic Chemistry*, G. Wilkinson, G.F.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 1, p. 475, 1982.

[44] H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, **18** (1980) 99.

[45] J.N. Hay and R.M.S. Obaid, *Eur. Polym. J.*, **14** (1978) 965.

[46] K.H. Reichert and K.R. Meyer, *Makromol. Chem.*, **169** (1973) 163.

[47] R. Ishioka and T. Sasaki, *Kagaku Keizai*, May (1990) 84.

[48] N. Kashiwa and M. Kioka, *Kagaku Kogyo*, **36** (1985) 523.

[49] N. Kashiwa, A. Toyota and M. Kioka, *Nikakyo Geppo*, July (1985) 17.

[50] H. Kineshima, N. Kashiwa, H. Koda, M. Ichimura and A. Kato, *Kagaku Kogaku*, **50** (1986) 377.

[51] N. Kashiwa and A. Toyoda, *Kagaku Keizai*, October (1986) 18.

[51a] V.R. Jensen, M. Ystenes, K. Wärnmark, B. Åkermark, M. Svensson, P.E.M. Siegbahn and M.R.A. Blomberg, *Organometallics*, **13** (1994) 282.

[51b] H.J. Kakkonen, J. Pursiainen, T.A. Pakkanen, M. Ahlgrén and E. Iiskola, *J. Organomet. Chem.*, **453** (1993) 175.

[51c] M. Bochmann, A.J. Jaggar and J.C. Nicholls, *Angew. Chem. Int. Ed. Engl.*, **29** (1990) 780.

[51d] P.C. Möhring, N. Vlachakis, N.E. Grimmer and N.J. Coville, *J. Organomet. Chem.*, **483** (1994) 159.

[51e] E.P. Bierwagen, J.E. Bercaw and W.A. Goddard, *J. Am. Chem. Soc.*, **116** (1994) 1481.

[51f] J.J. Eisch, S.I. Pombrik and G.-X. Zheng, *Organometallics*, **12** (1993) 3856.

[52] G.W. Parshall, W.A. Nugent, D.M.-T. Chan and W. Tam, *Pure Appl. Chem.* **57** (1985) 1809.

[53] J.E. McMurry, *Acc. Chem. Res.*, **16** (1983) 405.

[54] J.-M. Pons and M. Santelli, *Tetrahedron*, **44** (1988) 4295.

[55] D. Lenoir, *Synthesis*, (1989) 883.

[56] J.E. McMurry, *Chem. Rev.*, **89** (1989) 1513.

[57] Y. Dang and H.J. Geise, *J. Organomet. Chem.*, **405** (1991) 1.

[58] H. Yamamoto and A. Mori, *Kagaku Zokan*, **105** (1985) 63.

[59] K. Narasaka, *Kagaku Zokan*, **96** (1982) 37.

[60] A. Nakamura and H. Yasuda, *Kagaku*, **40** (1985) 359.

[61] Y. Yamamoto, *Kagaku*, **40** (1985) 364.

[62] T. Kukaiyama, M. Hayashi and K. Narasaka, *Chem. Lett.* (1973) 291.

[63] T. Mukaiyama, T. Sato and J. Hanna, *Chem. Lett.*, (1973) 1041.

[64] J.E. McMurry and M.P. Fleming, *J. Am. Chem. Soc.*, **96** (1974) 4708.

[65] R. Dams, M. Malinowski, I. Westdorf and H.Y. Geise, *J. Org. Chem.* **47** (1982) 248.
[66] R.S.P. Coutts, P.C. Wailes and R.L. Martin, *J. Organomet. Chem.*, **50** (1973) 145.
[67] H. Ledon, I. Tkatchenko and D. Young, *Tetrahedron Lett.*, (1979) 173.
[68] Y. Handa and J. Inanaga, *Tetrahedron Lett.*, (1987) 5717.
[69] Y. Zhang and T. Liu, *Synthetic Commun.*, **18** (1988) 2173.
[70] M. Mori, Y. Uozumi and M. Shibasaki, *Tetrahedron Lett.*, (1987) 6187.
[71] A. Yamamoto, S. Go, M. Ookawa, M. Takahashi, S. Ikeda and T. Keii, *Bull. Chem. Soc. Japan*, **45** (1972) 3110.
[72] F. Sato, S. Iijima and M. Sato, *J. Chem. Soc. Chem. Commun.*, (1981)180.
[73] H.G. Alt and H.E. Engelthardt, *J. Am. Chem. Soc.*, **107** (1985) 3717.
[74] H.G. Alt, G.S. Herrmann, M.D. Rausch and D.T. Mallin, *J. Organomet. Chem.*, **356** (1988) C53.
[74a] W.A. Nugent and J.C. Calabrese, *J. Am. Chem. Soc.*, **106** (1984) 6422.
[74b] S.C. Berk, R.B. Grossma and S.L. Buchwald, *J. Am. Chem. Soc.*, **116** (1994) 8593.
[75] J.R. Stille and R.H. Grubbs, *J. Am. Chem. Soc.*, **108** (1986) 855.
[76] F.N. Tebbe, G.W. Parshall and G.S. Reddy, *J. Am. Chem. Soc.*, **100** (1978) 3611.
[77] T.R. Howard, J.B. Lee and R.H. Grubbs, *J. Am. Chem. Soc.*, **102** (1980) 6876.
[78] K. Takai, Y. Hotta, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, (1978) 2417.
[79] M. Iyoda, T. Kushida, S. Kitami and M. Oda, *J. Chem. Soc. Chem. Commun.*, (1987) 1607.
[80] S.H. Pine, R. Zahler, D.A. Evans and R.H. Grubbs, *J. Am. Chem. Soc.*, **102** (1980) 3270.
[81] M.T. Reetz, J. Westermann and R. Steinbach, *J. Chem. Soc. Chem. Commun.*, (1981) 237.
[82] B. Weidmann, L. Widler, A.G. Olivero, C.D. Maycock and D. Seebach, *Helv. Chim. Acta*, **64** (1981) 357.
[83] M.T. Reetz, R. Steinbach, J. Westermann and R. Peter, *Angew. Chem. Int. Ed. Engl.*, **19** (1980) 1011.
[84] A.G. Olivero, B. Weidmann and D. Seebach, *Helv. Chim. Acta*, **64** (1981) 2485.
[85] R.O. Duthaler and A. Hafner, *Chem. Rev.*, **92** (1992) 807.
[86] A. Hafner, R.O. Duthaler, M. Marti, G. Rihs, P. Rothe-Streit and F. Schwarzenbach, *J. Am. Chem. Soc.*, **114** (1992) 2321.
[87] R.D. Broene and S.L. Buchwald, *J. Am. Chem. Soc.*, **115** (1993) 12569.
[88] A.L. Costa, M.G. Piazza, E. Tagliavini, G. Trombini and A. Umani-Ronchi, *J. Am. Chem. Soc.*, **115** (1993) 7001.
[89] M.B. Carter, B. Schiøtt, A. Gutiérrez and S.L. Buchwald, *J. Am. Chem. Soc.*, **116** (1994) 11667.
[90] C.A. Willoughby and S.T. Buchwald, *J. Am. Chem. Soc.*, **116** (1994) 11703.

13 Organochromium Compounds

13.1 INTRODUCTION

Speaking of organochromium compounds, the Hein complex ((η^6-(C_6H_6))$_2$Cr), discovered in 1919, is well known. From the example of the Hein complex, chromium is an element which is able to form a stable π-complex with aromatic ring compounds. If an aromatic compound coordinates with the chromium atom, the aromatic compound shows a different reactivity since the electronic state of the aromatic compound becomes different. The synthesis of organochromium compounds is easy and handling is also easy since many compounds are stable. The chromium complexes are used as organosynthetic reagents, since specific reactions tend to proceed. This chapter describes mainly the applications of organosynthetic reagents from organochromium compounds.

13.2 CHROMIUM

Chromium exists in 100 ppm in the Earth's crust, in amounts similar to those of zinc and copper [1]. Chromite ($FeO \cdot Cr_2O_3$) is the main ore. Chromium is produced by the electrolysis or the reduction of chromium oxide with metals [2–6].

The electrolysis process is performed first, by mixing chromite ($FeO \cdot Cr_2O_3$), carbon and lime as the flux in an electric furnace, and the mixture is heated to give a ferrochromium. The ferrochromium is dissolved in sulfuric acid near its boiling point, ammonium sulfate is added, then the slurry is cooled to 80 °C or below, and the undissolved solids, mostly silica, are separated by filtration. The solution is cooled to 5 °C to precipitate ferrous ammonium sulfate ($((NH_4)_2SO_4 \cdot FeS)_4 \cdot 6H_2O$). The mother liquor is left at *ca.* 30 °C for a long time to precipitate ammonium chrome alum ($NH_4Cr(SO_4)_2$). The chrome alum is filtered, washed and dissolved in hot water. The solution is electrolyzed to give 99.8% pure chromium metal [5].

The reduction process with chromium oxide comprises of, first, mixing chromite, soda ash (Na_2CO_3) and slaked lime ($Ca(OH)_2$) in a rotary kiln, and roasting them to give sodium chromate (Na_2CrO_4) (eq. (13.1)). Sulfuric acid is added to the

$$2FeO \bullet Cr_2O_3 + 4Na_2CO_3 + 4Ca(OH)_2 \xrightarrow{O_2} 4Na_2CrO_4 + Fe_2O_3 + 4CaCO_3 + 4H_2O \quad (13.1)$$

sodium chromate to give sodium dichromate ($Na_2Cr_2O_7{\cdot}2H_2O$) and sodium sulfate (eq. 13.2). Sodium sulphate is allowed to precipitate and separated, and the mother liquor is filtered and kept under cool conditions to precipitate sodium dichromates. The sodium dichromate is reduced by heating with sulfur, charcoal or ammonium chloride, and is washed with water for removal of the soluble salt, filtered, dried and chromium oxide is produced as shown in eqs. (13.3)–(13.5). Chromium metal is produced by the reduction of chromium oxide with aluminum or silicon. Using aluminum as the reducing agent, the reaction proceeds continuously without heating since the reduction is exothermic. A mixture of aluminum powder and chromium oxide is heated in advance, barium peroxide and magnesium powder are added and the mixture is ignited. The purity of the chromium is 97–98%. Using silicon as the reducing agent, the reaction heat is small compared to that with aluminum, and so the reaction proceeds with heating in an electric arc furnace. The product is similar to that obtained by the aluminothermic process; however, the aluminum content is lower and silicon may run as high as 0.8%.

$$2Na_2CrO_4 + H_2SO_4 + H_2O \longrightarrow Na_2Cr_2O_7{\bullet}2H_2O + Na_2SO_4 \quad (13.2)$$

$$Na_2Cr_2O_7 + S \longrightarrow Cr_2O_3 + Na_2SO_4 \quad (13.3)$$

$$Na_2Cr_2O_7 + 2C \longrightarrow Cr_2O_3 + Na_2CO_3 + CO \quad (13.4)$$

$$Na_2Cr_2O_7 + 2NH_4Cl \longrightarrow Cr_2O_3 + 2NaCl + N_2 + 4H_2O \quad (13.5)$$

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 \quad (13.6)$$

Chromium is an element which belongs to group 6 of the periodic table, and the outer electron configuration is $5d^54s^1$. When the $4s^1$ electron forms a complex, as it is favorable for the electron to go into a 3d orbital and bond with a ligand, the d electron of the chromium (0) complex should be thought of as having six electrons. Organometallic complexes tend to form a bond in accordance with the eighteen-electron rule. Therefore, chromium tends to bond with compounds which donate a total of twelve electrons. As benzene is able to donate six electrons and carbonyl is able to donate two electrons, the chromium complex of both $(\eta^6\text{-}(C_6H_6))_2Cr$ and $\eta^6\text{-}(C_6H_6)Cr(CO)_3$ has 18 electrons and these complexes are stable at ordinary temperatures.

Chromium dissolves in nonoxidizing mineral acids, such as hydrochloric acid, dilute sulfuric acid, hydrofluoric acid, but not in aqua regia, concentrated nitric acid, phosphoric acid, chloric acid and perchloric acid, which passivate the metal.

Table 13.1 Physical properties of chromium [2–4]

Property	Value
melting point, °C	1857
boiling point, °C	2672
crystal structure	body-centered cubic
density, 20 °C, g/cm^3	7.19
specific heat at 25 °C, J mol^{-1}K^{-1}	23.25
heat of fusion, kJ/mol	16.93
latent heat of vaporization at bp, kJ/mol	344.3
linear coefficient of thermal expansion at 20 °C	6.2×10^{-6}
resistivity at 20 °C, W m	12.9×10^{-8}
thermal conductivity at 20 °C, W m^{-1}K^{-1}	67
ionization potential, V	
1st	6.74
2nd	16.6

The properties of chromium are shown in Table 13.1 [2–4]. Chromium is used as an additive metal for superalloy since it has a high melting point and a high resistance to oxidation. Stainless steel is an alloy in which metals such as Ni, Mo, Ti and Nb are added to a chrome steel containing 12% or more chrome. For example, 18-8 stainless steel is steel containing 18% of Cr and 8% of Ni. The other uses are as additives to the various kind of superacid resisting alloys [2–4]. Sodium dichromate ($Na_2Cr_2O_7$) is used as a tanning agent and potassium dichromate ($K_2Cr_2O_7$) is used as the raw material for pigments, mordants and oxidizing agents. Chromium oxide (Cr_2O_3) is used as a magnetic recording material, etc. [5].

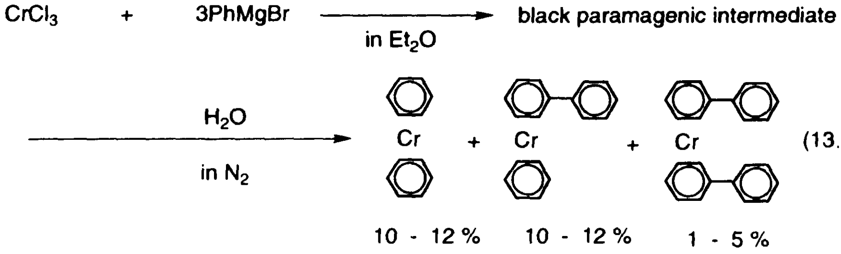
13.3 PREPARATION OF ORGANOCHROMIUM COMPOUNDS

Organochromium compounds form the various kinds of compounds shown in Table 13.2 described in the next section. The most representative compounds are two compounds of $(\eta^6\text{-}(C_6H_6))_2Cr$ and $\eta^6\text{-}(C_6H_6)Cr(CO)_3$. The synthetic methods for these compounds are described below [7,8].

13.3.1 GRIGNARD SYNTHESIS

Grignard synthesis is the method that Hein [9] used first to synthesize organochromium compounds in 1919. Anhydrous chromium chloride reacts with PhMgBr in an ether solution, forming an inflammable, paramagnetic black solid. Phenylchromium compound is obtained by hydrolysis of the black solid.

As described in Chapter 2, in the history of organometallic compounds, at that time, the ferrocene π-complex was not known. The compound is thought to be a σ-complex and in 1954 Zeiss [10] found that the compound is a π-complex shown in eq. (13.7)



(13.7)

Anhydrous chromium chloride reacts with PhMgBr in tetrahydrofuran to yield a red crystal. The crystal is such that the chromium is coordinated with three molecules of THF and bonds to three phenyl groups. The red crystal is changed to the black solid shown in eq. (13.7) by adding ether, under vacuum or heating, and furthermore the same product as from the ether reaction product is obtained by hydrolysis [11]. From the reactions shown in eqs. (13.7) and (13.8), the reaction in eq. (13.7) shows that the rearrangement of a σ-complex to π-complexes proceeds. The black solid is thought of as follows: two phenyl groups of three phenyl groups of $Ph_3Cr(OC_4H_8)_3$ couple to form biphenyl, and benzene is formed by the hydrogenation of one phenyl group. The second product (eq. (13.7)) is π-complex of this biphenyl and benzene. The black solid is mainly this second product and by hydrolysis with partial disproportionation gives $(\eta^6\text{-}(C_6H_6))_2Cr$ and $(\eta^6\text{-}(C_6H_5\text{-}C_6H_5)_2Cr$ [8,11–13].

$$\mathrm{CrCl_3} + \mathrm{3PhMgBr} \xrightarrow[\text{in THF}]{-25^\circ\mathrm{C}} \underset{\text{red crystal}}{\mathrm{Ph_3Cr(OC_4H_8)_3}} \xrightarrow{\mathrm{Et_2O},\ \text{or vac., or heat}} \text{black paramagnetic intermadiate} \qquad (13.8)$$

With various kinds of ArMgBr and tetrahydrofuran complexes it is synthesized by the reaction shown in eq. (13.8), and the various kinds of π-aryl complexes are produced by rearrangement. However, Grignard reactions tend to produce the mixed products when the aryl ring bonds to alkyl or aryl groups since Grignard reagents accompany the rearrangement. Furthermore, the reaction with ortho aryl derivatives and haloaryl derivatives are difficult to proceed. Therefore, Grignard reagents are not suitable reagents to produce a single π-complex in high yield [8].

13.3.2 FISHER–HAFNER SYNTHESIS

Fisher and Hafner [14] found the synthesis of π-aryl complexes with aromatic compounds, chromium chloride, aluminum chloride and aluminum metal in 1955 as shown in eq. (13.9). These mixture is heated to afford bisaryl cation, and bisaryl complexes are prepared by reduction with water soluble sodium dithionite ($Na_2S_2O_4$). $(\eta^6\text{-}(C_6H_6))_2Cr$ is isolated as a dark brown material by sublimation by heating under a high vacuum [15].

$$3CrCl_3 + 6C_6H_6 + 2Al + AlCl_3 \xrightarrow{140^\circ - 150\ ^\circ C,\ 15\ h} 3(\eta^6\text{–}C_6H_6)_2Cr^+(AlCl_4)^-$$

$$2[(\eta^6\text{–}C_6H_6)_2Cr]^+ + S_2O_4^{2-} + 4OH^-$$

$$\longrightarrow 2[(\eta^6\text{–}C_6H_6)_2Cr] + 2SO_3^{2-} + 2H_2O \qquad (13.9)$$

mp 284 - 285 °C
dc 300 °C
yield 50 %

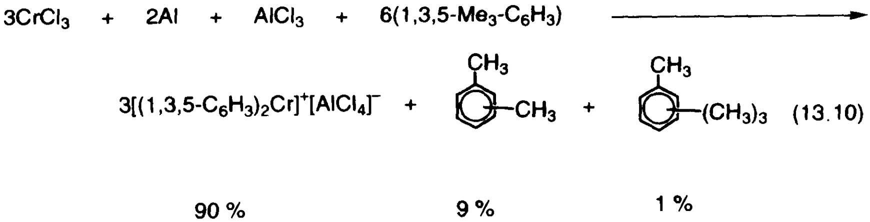
With molybdenum and tungsten compounds from the same group as chromium, similar reactions proceed. Their reactivities are very low and the order of these reactivities are as follows:

$$Cr > Mo > W$$

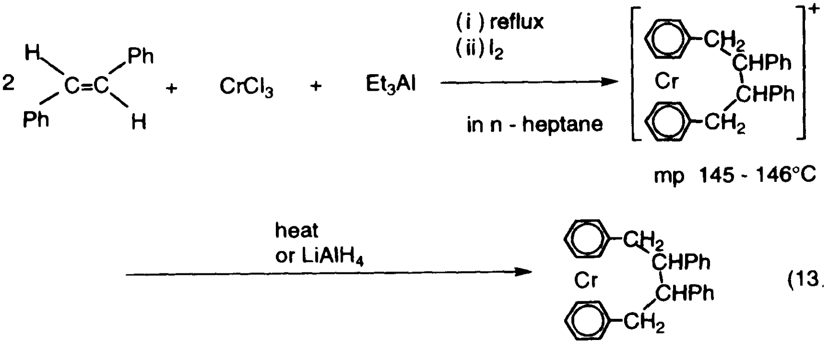
In the Fisher–Hafner synthesis, the reactivity of aromatic compounds having an electron donating substituent is high since the π-electron of the aromatic ring is liable to react with the chromium atom. For example, mesitylene ($1,3,5\text{-}Me_3C_6H_3$), bonded by three methyl groups which are electron donating groups, is more reactive than benzene. The ligand exchange reaction of the aromatic ring in the Fisher–Hafner synthesis is liable to proceed by the action of aluminum chloride. Therefore, in the reaction of benzene with chromium chloride as shown in eq. (13.9) with a small amount of mesitylene, firstly the reactive mesitylene reacts with chromium chloride to produce $(\eta^6\text{-}(1,3,5\text{-}Me_3C_6H_3))_2Cr$ immediately, with $(\eta^6\text{-}(C_6H_6))_2Cr$ produced by the ligand exchange reaction with benzene. That is, mesitylene acts as the catalyst for the reaction of benzene with chromium chloride. $(\eta^6\text{-}(C_6H_6))_2Cr$ is prepared in high yield at low temperatures in the presence of a small amount of mesitylene [8].

The Fisher–Hafner synthesis is the convenient synthetic method for various kinds of $(\eta^6\text{-}(\text{arene}))_2Cr$ type compounds, since it yields a single product different from the Grignard synthesis. However, precautions should be taken on compounds on which transalkylations or isomerization tends to proceed [16]. For example, mesitylene is reactive as described above in that a transalkylation partly proceeds to afford xylene and tetramethylbenzene. The transalkylation such as the reaction with mesitylene, is depressed by reagents of $CrBr_3/AlBr_3/Al$ type [16]. Further, the reaction with Et_3Al in place of $AlCl_3/Al$ as a reducing agent proceeds at low temperatures and the ratio of rearrangement or fission reaction is low [8,17].

Reaction with trans-stilbene does not afford simply $(\eta^6\text{-(arene)})_2Cr$, but reductive cyclic dimerization proceeds as shown in eq. (13.11) [18].



(13.10)



(13.11)

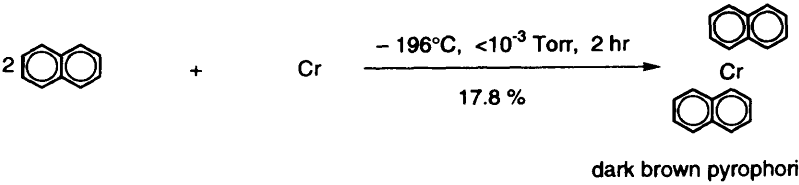
13.3.3 METAL VAPOR SYNTHESIS

Metal vapor synthesis was developed in 1919 by Timms [19,20]. The reaction vessel is cooled with liquid nitrogen, then evacuated at 10^{-4}–10^{-6} Torr, then chromium metal is evaporated by heating at 1300–1700 °C with molybdenum filaments and aromatic compounds react with gaseous chromium. For example, $(\eta^6\text{-}(C_6H_6))_2Cr$ is prepared in 60% yield as shown in eq. (13.12) [19].

$$\underset{\text{vapor}}{2C_6H_6} + \underset{\text{vapor}}{Cr} \xrightarrow[\text{in liq. } N_2]{} \underset{60\%}{(\eta^6\text{-}C_6H_6)_2Cr} \qquad (13.12)$$

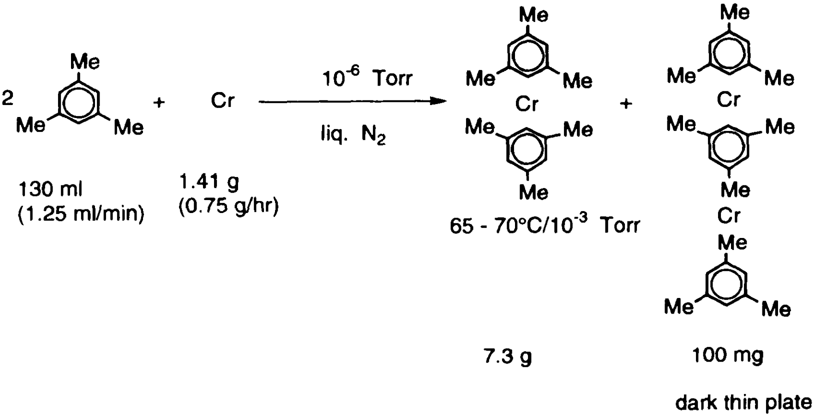
Metal vapor synthesis is liable to synthesize compounds from aromatic compounds having an electron-withdrawing group such as F, Cl, OMe, COOMe and CF_3, or compounds which are difficult to synthesize by the Fisher–Hafner reactions since transalkylation is liable to proceed. Metal vapor synthesis tends to afford a high purity of $(\eta^6\text{-(arene)})_2\text{Cr}$ [8,21,22]. In the case of molybdenum and tungsten, the reaction is difficult since their boiling point is high and the vaporization of the metals is difficult [7].

Aromatic compounds used are benzene, naphthalene, 1,4-diphenylbutane, etc. Various kinds of $(\eta^6\text{-(arene)})_2\text{Cr}$ have been synthesized. For example, reaction with naphthalene is shown in eq. (13.13) [23].



(13.13)

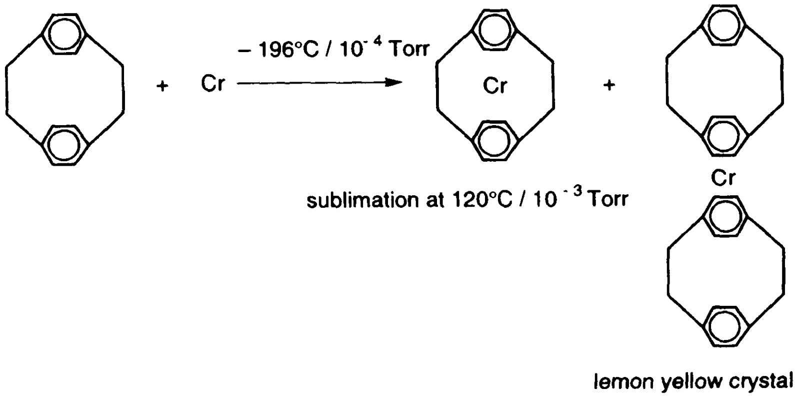
In the case of mesitylene, it reacts with chromium at 10^{-6} Torr by heating with tungsten filaments to afford a triple-decker sandwich complex (see Figure 13.2) besides $(\eta^6\text{-}(1,3,5\text{-MeC}_6\text{H}_3))_2\text{Cr}$ as shown in eq. (13.14) [24].



(13.14)

Reaction with [2.2]paracyclophane affords the two kinds of sandwich compounds shown in eq. (13.15). One is η^{12}-[2.2]-paracyclophanechromium and the other is bis(η^6-[2.2]-paracyclophane)chromium [25,26].

The distance between the two benzene rings of $(\eta^6\text{-}(\text{C}_6\text{H}_6))_2\text{Cr}$ is 3.22 Å. However, the distance between the two benzene rings of η^{12}-[2.2]-paracyclophanechromium is only about 2.90 Å. Hence η^{12}-[2.2]-paracyclophanechromium forms the compressed sandwich structure, likely to be compressed with an ethylene chain [27]. Therefore, η^{12}-[2.2]-paracyclophanechromium is very stable compared with bis(η^6-[2.2]-paracyclophane)-chromium, it is not affected in concentrated hydrochloric acid for a week or more [25].



(13.15)

13.3.4 REPLACEMENT REACTIONS

The most basic organochromium compounds are hexacarbonylchromium compounds as shown in eq. (13.16). Many organochromium compounds are prepared by ligand exchange reactions (replacement reactions) of the carbonyl group of hexacarbonylchromium shown in eqs. (13.17)–(13.22) [25–31].

Hexacarbonylchrominum is easily synthesized by the reaction of carbon monoxide with chromium chloride or triacetylacetonatechromium and reducing agents such as Al/AlCl$_3$, Grignard reagents, Mg, LiAlH$_4$, Na, K and Et$_3$Al [15,28,32–34]. The reaction shown in eq. (13.16) shows Al/AlCl$_3$ as the reducing agent and the

$$CrCl_3 \quad + \quad 6CO \xrightarrow[150-200\ \text{atm},\ 10\ \text{h}]{Al/AlCl_3,\ 140-150^\circ C} \underset{88\ \%}{Cr(CO)_6} \qquad (13.16)$$

reaction with Et$_3$Al as the reducing agent afford hexacarbonylchromium in a high yield (93%) [33]. Hexacarbonylchromium is stable in air and is a colorless volatile solid. The solid melts in air at 130 °C with decomposition and its replacement reaction, that is, the ligand exchange reaction, easily proceeds with the various kinds of compounds as shown in eq. (13.17).

$$Cr(CO)_6 \quad + \quad nL \xrightarrow{\qquad\qquad} Cr(CO)_{6-n}L_n \qquad (13.17)$$

$$L = NR_3,\ \text{pyridine},\ PR_3,\ AsR_3,\ \text{etc.}$$

The ligand exchange reactions with molybdenum and tungsten hexacarbonyl compounds also proceed as shown in eq. (13.17). Reactions with phosphine are shown in eq. (13.18) [29].

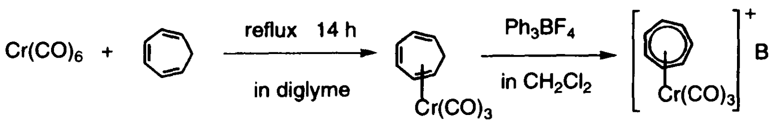
$$\mathrm{M(CO)_6} + n\,\mathrm{PR_3} \longrightarrow \mathrm{M(CO)_{6-\mathit{n}}(PR_3)_{\mathit{n}}} \quad (13.18)$$

$$\mathrm{M} = \mathrm{Cr, Mo, W}; \quad \mathrm{R} = \mathrm{Et, Ph}; \quad n = 1, 2, 3$$

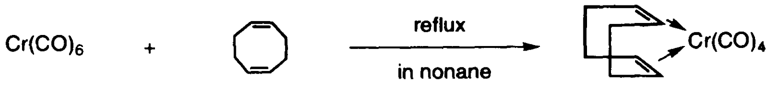
If the ligand is an unsaturated compound, generally, they are liable to be exchanged with three carbonyl groups. For example, a reaction with benzene affords η^6-$(C_6H_6)Cr(CO)_3$ as shown in eq. (13.19). But, in the case that it is sterically hindered then chromium is coordinated with three double bonds, e.g., nonconjugated diene (eq. (13.21)) or tetracyanoethylene (eq. (13.22)), one or two carbonyl groups are liable to be exchanged.

$$\mathrm{Cr(CO)_6} + \mathrm{C_6H_6} \xrightarrow[\text{in diglyme}]{\text{reflux, 9 h}} (\eta^6\text{-}\mathrm{C_6H_6})\mathrm{Cr(CO)_3} \quad (13.19)$$

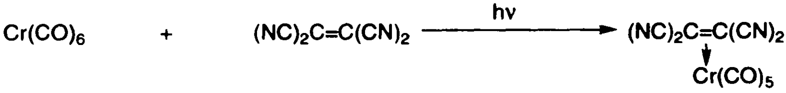
bp 80 - 85°C / 10^{-3} Torr
mp 162 - 163°C



(13.20)



(13.21)



$$\mathrm{Cr(CO)_6} + \mathrm{(NC)_2C{=}C(CN)_2} \xrightarrow{h\nu} \underset{\displaystyle \mathrm{Cr(CO)_5}}{\underset{\downarrow}{\mathrm{(NC)_2C{=}C(CN)_2}}} \quad (13.22)$$

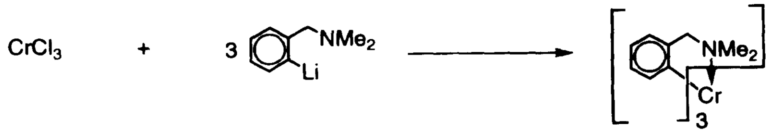
These reactions does not show a high yield since hexacarbonylchromium is a volatile compound (sublimation). However, with the apparatus in which sublimated hexacarbonylchromium is continuously put back into the original flask, the yield increases. For example, the reaction of benzene shown in eq. (13.19) with this apparatus affords η^6-$(C_6H_6)Cr(CO)_3$ in 97% yield [15,34]. The η^6-$(C_6H_6)Cr(CO)_3$ is a volatile yellow crystal, and is stable to moisture or oxygen.

13.3.5 OTHERS

The other syntheses of organochromium compounds are the reactions of chromium chloride with organoalkali metal compounds. For example, chromocene (bis-(η^5-cyclopentdienyl)chromium) is easily prepared in high yield by the reaction of chromium chloride with cyclopentadienylsodium in tetrahydrofuran as shown in eq. (13.23) [15,35].

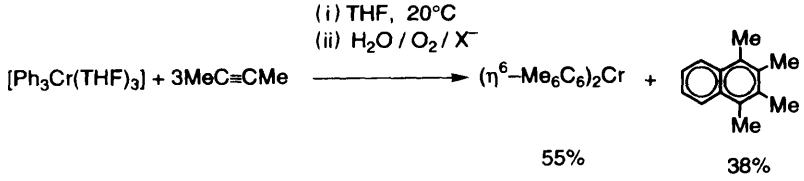
$$CrCl_3 + 3C_5H_4Na \xrightarrow[\text{in THF}]{} \underset{\text{mp } 173^\circ C}{(\eta^5\text{-}C_5H_5)_2Cr} + 3Na + C_5H_5 \qquad (13.23)$$

The cyclometalation of *o*-lithium dimethylaminobenzene with chromium chloride proceeds to give the five-membered ring as shown in eq. (13.24) [26,36]. Many organometallic intramolecular-coordination compounds containing the five-membered ring structure of organochromium compounds have been synthesized and the structure was determined by X-ray diffraction studies as shown in the book *Organometallic Intramolecular-coordination Compounds* [26].



(13.24)

As the other reaction method, trialkyl or triarylchromium compounds react with acetylene compounds to give (η^6-(arene))$_2$Cr by a cycliccondensation as shown in eq. (13.25) [8,37–40].



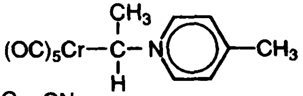
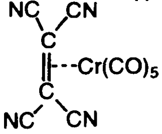
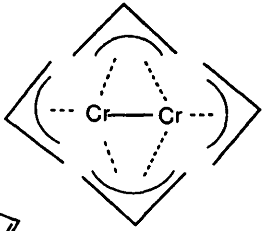
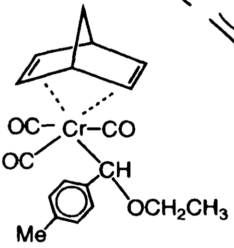
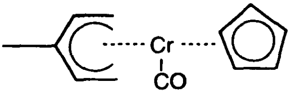
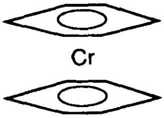
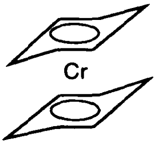
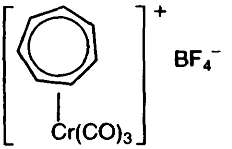
(13.25)

13.4 STRUCTURES OF ORGANOCHROMIUM COMPOUNDS

(η^6-(C_6H_6))$_2$Cr is an 18-electron compound as described above and it forms a sandwich structure. An element which is able to form a π-complex with benzene is not only Mo and W, from the same group, but also Ti, Zr, V, Nb, Ta, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pt, Pd, Cu and Ag [7]. As for organochromium compounds besides six π-electron complexes η^6 with benzene, η^1 to η^7 compounds are shown in Table 13.2 [8,29].

The structure of (η^6-(C_6H_6))$_2$Cr has been reported as having two forms: one is D_{6h} when all CC bonds are the same, the other is bent D_{3d} when there are two kinds of CC bonds [41–48]. At 100 K, the CC bond is 1.417 Å long and the symmetry is D_{6h} [46]. However, neutron diffraction analysis indicated a D_{3h} symmetry with alternating long (1.424 Å) and short (1.406 Å) ring CC bond lengths. As the CC bond of solid benzene is 1.397 Å, all CC bonds coordinated to chromium are

Table 13.2 Structures of organochromium [8,29,29a,29b,29c]

η^n	Compound
η^1	 Cr – C = 2.250 Å
η^2	
η^3	
η^4	
η^5	
η^6	 C - C : 1.417 Å D_{6h}  D_{3d} C - C : 1.406 Å, 1.424 Å
η^7	

elongated. From these data, the benzene ring coordinated to chromium is considered to have decreased aromaticity [8].

η^6-$(C_6H_6)Cr(CO)_3$ is called a piano-stool structure. Figure 13.1, according to neutron diffraction analysis, shows the structure at 78 K by looking up from the bottom of the piano-stool. The CC bond length in the benzene ring *trans* to the carbonyl group is slightly shorter. The benzene ring has a planar structure [48]. If the benzene ring of η^6-$(C_6H_6)Cr(CO)_3$ bonds with the substituent electron donating or electron-withdrawing groups, as shown in Scheme 13.1, the benzene ring forms a resonance structure with an exocyclic double bond. Namely, the *ispo* carbon (the carbon bonded with the substituent group) forms an sp^2 structure and the benzene ring forms a bent structure. If an electron-donating group bonds to the benzene ring, the chromium atom having 18 electrons repels the electron of the exocyclic double bond, and the double bond bends to the other side of the chromium atom. On the other hand, if an electron-withdrawing group bonds to the benzene ring, the chromium bonds with the π-electron of the exocyclic double bond, and the double bond bends to the inner side of the chromium atom [49,50].

The triple-decker sandwich structure of η^6-$(1,3,5\text{-}C_6H_6)_3Cr_2$ (eq. (13.14)) is shown in Figure 13.2. Three benzene rings are parallel and perfectly eclipsed. The distance from Cr to the terminal ring plane is 1.600 Å. This is comparable to the Cr–ring distance of 1.609 Å found in bis(benzene)chromium [46]. The distance from Cr to the central ring plane is slightly long at 1.669 Å. The CC bond distances of the three rings are close to those of $(\eta^6$-$(C_6H_6))_2Cr$ [51,52]. Namely, the decrease in three ring aromaticity is thought to be almost the same as that of $(\eta^6$-$(C_6H_6))_2Cr$.

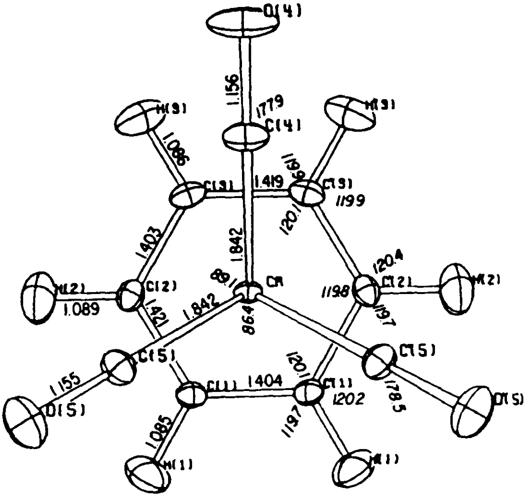
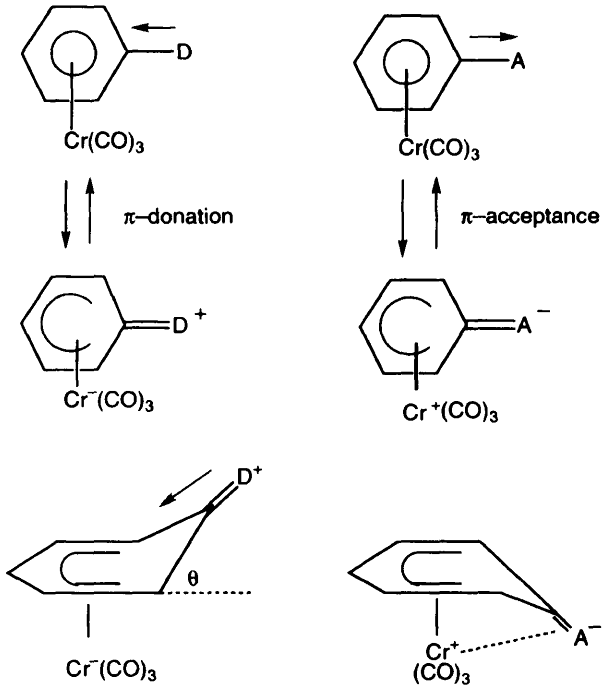


Figure 13.1 Bond lengths and angles in $(\eta^6$-$C_6H_6)Cr(CO)_3$ according to the neutron analysis [48].



D = donor group : NEt_2 θ = 5.89°
NH_2 θ = 5.78°

A = acceptor group : COMe θ = − 1.04°

Scheme 13.1 [49,50]

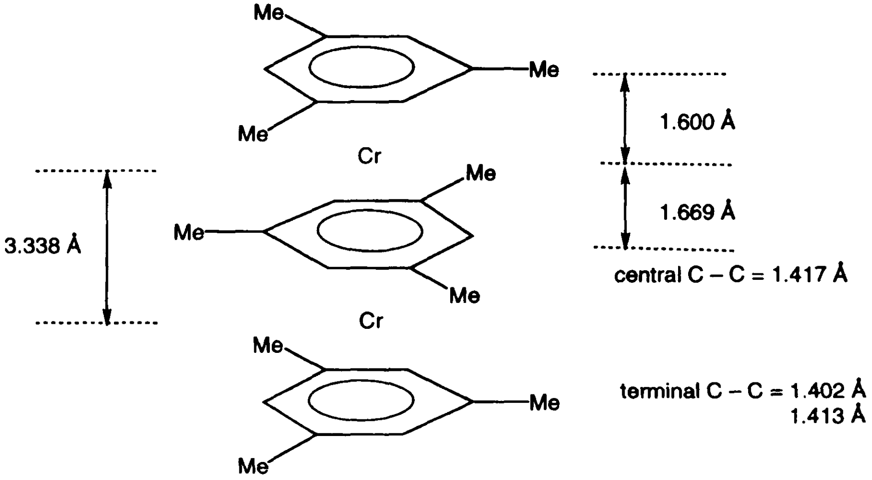


Figure 13.2 Structure of tris(mesitylene)dichromoium [51].

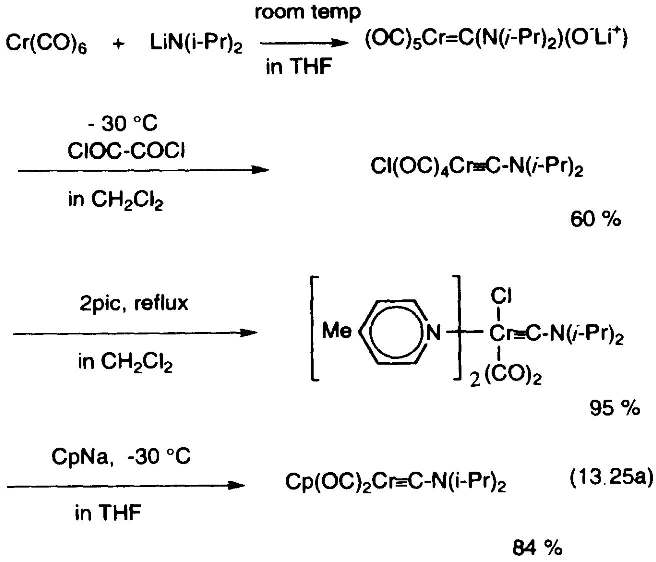
Carbene is a liable intermediate in organic reactions; however, if it coordinates to a transition element, the coordination bond is stable and it is able to be isolated as a complex. Singlet carbene ($:CX_2$) forms an sp^2 hybrid orbital, has six electrons with two p-orbitals, and a third orbital remains as vacant (p_z orbital). When the carbene forms a complex, lone pair electrons of one of the sp^2 hybrid orbitals σ-donates to the metal atom and π-electrons of the metal back-donate to the vacant orbital p_z of the carbon atom (σ-donation π-back donation). Therefore, this MC bond should thus exhibit partial double bond character. However, as the p_z vacant orbital which is used for back donation didn't have enough acceptor orbitals available for the back-donation process, the double bond character is thought to be small [53].

The bond lengths (Cr=C) of carbene complex are as follows:

$(OC)_5Cr{=}C(Ph)OMe$	2.04 Å
$(OC)_5Cr{=}C(Me)NHMe$	2.09 Å
$(Ph_3P)(OC)_4Cr{=}C(Me)OMe$	2.00 Å
$(OC)_5Cr{=}C(Me)NEt_2$	2.16 Å

As the sum of the covalent bond radii of CrC is 2.21 Å [52,53] (CrC in η^1 compounds is 2.250 Å in Table 13.2), these compounds form double bonds which are slightly shorter than that of the CrC single bond [53].

Recently, as shown in eq. (13.25a), the synthesis of carbyne complex from carbene complexes have been reported [53a]. The acetylene π-complex ([Cr(*t*-$C_4H_9HNC{\equiv}CNH$-*t*-C_4H_9)(CN-*t*-Bu)$_4$I]I, CCr = 1.937 Å, C=C = 1.367 Å) [53b], and two benzene sandwich structure bridged carbon chains or bridged manganesephosphine structures [53c,53d], etc. have been reported.



(13.25a)

13.5 REACTIONS OF ORGANOCHROMIUM COMPOUNDS

The various kinds of organochromium compounds are shown in Table 13.2. The main reactions of these compounds are ligand exchange reactions and reactions on the ligand. The reactions which show the characteristics of organochromium compounds are the latter reactions on the ligand. Namely, organic compounds react with chromium compounds to produce the organochromium compounds, and the reactions using the characteristics of the organochromium compounds are performed. Finally the desired compound is obtained by the elimination of the chromium atom from the organochromium compounds.

The reason that organochromium compounds are noteworthy in organosynthetic reaction is that aromatic compounds react with chromium carbonyl compounds such as $Cr(CO)_6$, $Cr(CO)_3(CH_3CN)_3$, $Cr(CO)_3(NH_3)_3$ to afford the organochromium compounds in high yields by simply heating under neutral reaction conditions, and finding the organochromium compounds are stable in air and after the reaction chromium metal is easily eliminated [54].

The other reason is that organochromium compounds are able to be formed by carbene complexes and the reaction of the carbene complexes are available.

13.5.1 REACTIONS WITH η^6-(ARENE)CHROMIUM$(CO)_3$

The most available reactions are reactions using the characteristics of η^6-(arene)$Cr(CO)_3$ as shown in Figure 13.3 [54–58b]. In the η^6-(arene)$Cr(CO)_3$ since the chromium metal bonded with three carbonyl groups of an electron-withdrawing group, is coordinated to the aromatic ring, and the electrons of the aromatic ring decrease and the aromatic ring itself and the hydrogen of alkyl group bonded to the aromatic ring show acidity. Therefore, the aromatic ring is liable to be attacked by a nucleophile, and nucleophilic addition and nucleophilic substitution tend to proceed. The alkyl groups are liable to solvolysis reactions. The reactions proceed stereospecifically since the reactions mainly proceed at a side with less steric hindrance because the aromatic ring is bonded with a bulky $Cr(CO)_3$ group [54–58b].

As shown in eq. (13.26), when a nucleophile reacts with η^6-$(C_6H_6)Cr(CO)_3$, the nucleophile adds to the carbon of the aromatic ring from the side (exo) which chromium does not bond to the aromatic ring, and a η^5-cyclohexadienylcarbonylchromium(0) complex is formed. The complex is stable between $-80\,^\circ C$ and $-30\,^\circ C$ and it is a yellow crystal. From the X-ray diffraction study, the five carbon atoms of the cyclohexyl ring form an approximately planar structure to form a coordination structure for chromium atoms, and the remaining carbon atom is located by bending 38.6° to the pentadienyl plane. An oxidizing agent such as iodine, Ce(IV) and oxygen reacts with this complex to afford an aromatic nucleophilic substitution product as shown in eqs. (13.26) and (13.27) [55,59]. But a strong acid reacts with the η^5-cyclohexadienylchromium complex to afford 1,3-diene by hydrogenation as shown in eq. (13.28). However, if a reagent such as BuLi

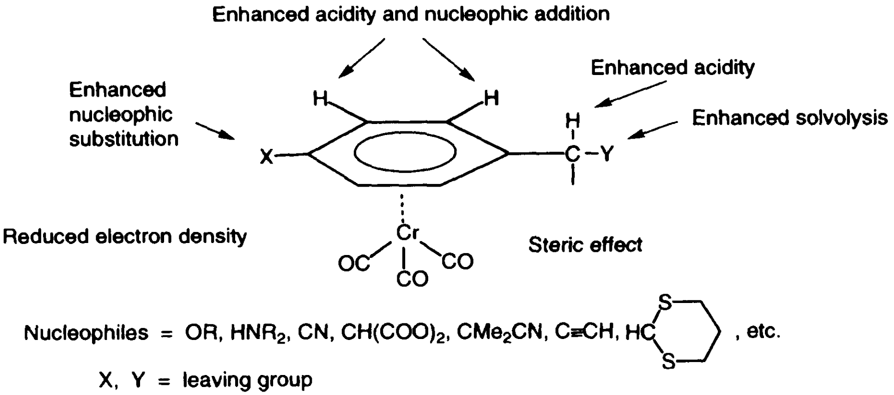
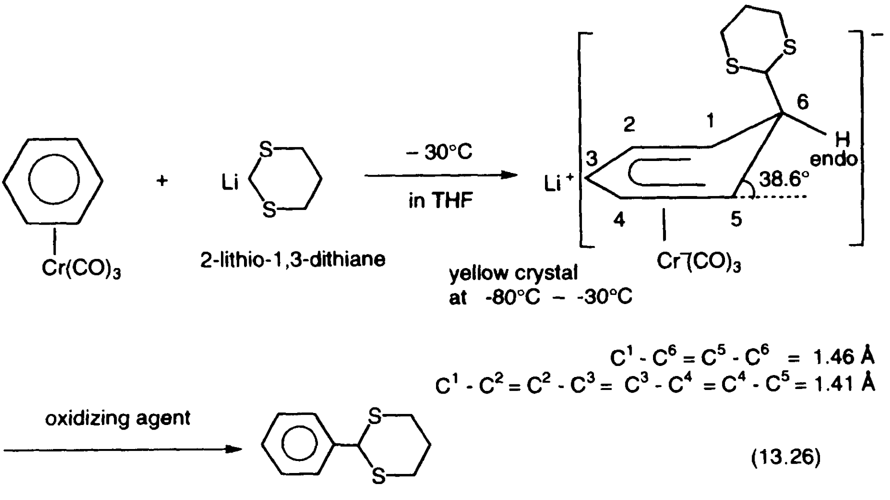


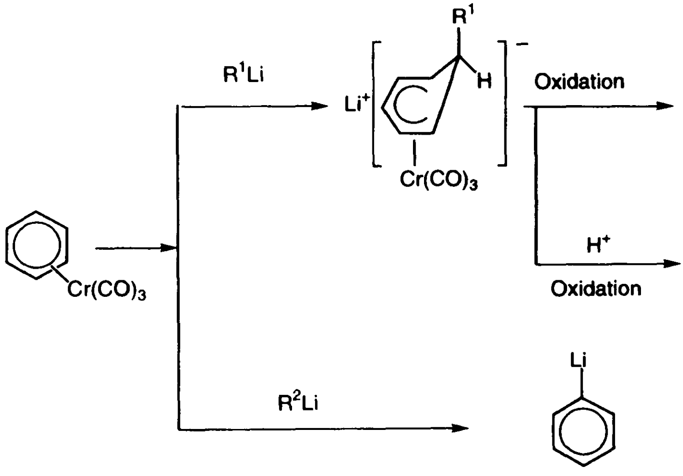
Figure 13.3 Effects on the reactivities of arenes coordinated to the chromium tricarbonyl [54–58].

and MeLi by which metalation is liable to proceed, is used as a nucleophilic reagent, the metalation reaction proceeds as shown in eq. (13.29). But, if the reagent is such like *t*-BuLi, for which the reactivity of metalation is not high, is used as the nucleophilic reagent, both of the reactions shown in eqs. (13.27) and (13.29) proceed and both η^5-cyclohexadienylchromium complex and the metalation product are obtained [55].



(13.26)

In the resonance structures of aromatic rings, the aromatic rings having a strong electron-donating substituent (RO, NR_2, F, etc.) show a meta-directing reactivity as shown in eq. (13.30) [55,60–63]. These aromatic compounds, which are not coordinated by chromium metal, show ortho-para orientation, and the reactions



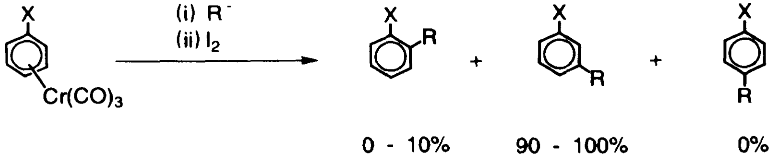
(13.27)

(13.28)

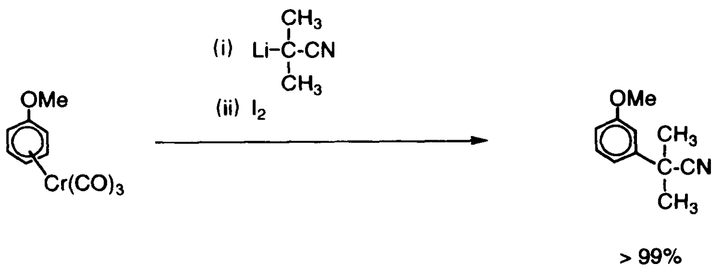
(13.29)

R^2Li = *n*-BuLi, MeLi, *s*-BuLi

shown in eq. (13.30) are quite different reactions from usual aromatic substitution reactions. The reaction shown in eq. (13.30) shows ordinarily 95% meta-direction, whereas the other forms ortho-substituted compound [55]. If the slightly bulky nucleophile of $LiC(CH_3)_2CN$ is used, 99% or more of the meta-substituted compound are obtained as shown in eq. (13.31) [55].

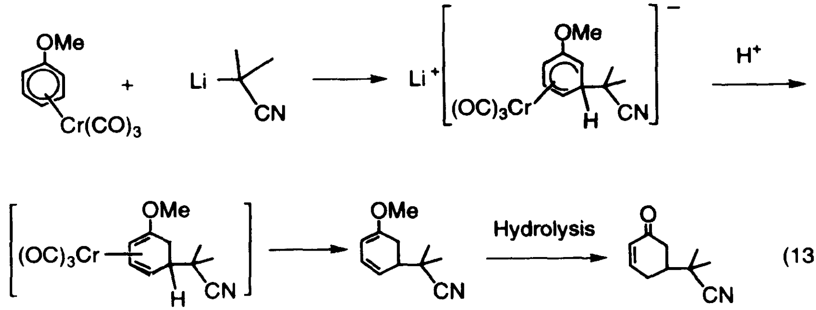


(13.30)



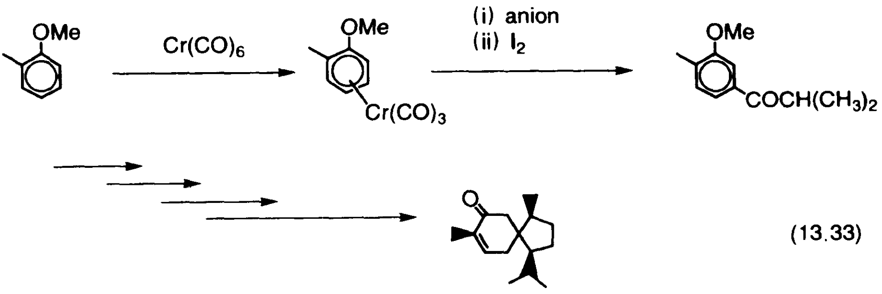
(13.31)

Cyclohexenone is prepared from anisole as a raw material by applying the meta-directing reaction (eq. (13.30)), oxidation with a strong acid as shown in eq. (13.28), and followed by hydrolysis as shown in eq. (13.32) [55]. These meta-



(13.32)

direction and the reduction reaction of organochromium compounds are used for the syntheses of various kinds of compounds. For example, the synthesis of the intermediate of sesquiterpene acorenone is shown in eq. (13.33) [61]. In the



(13.33)

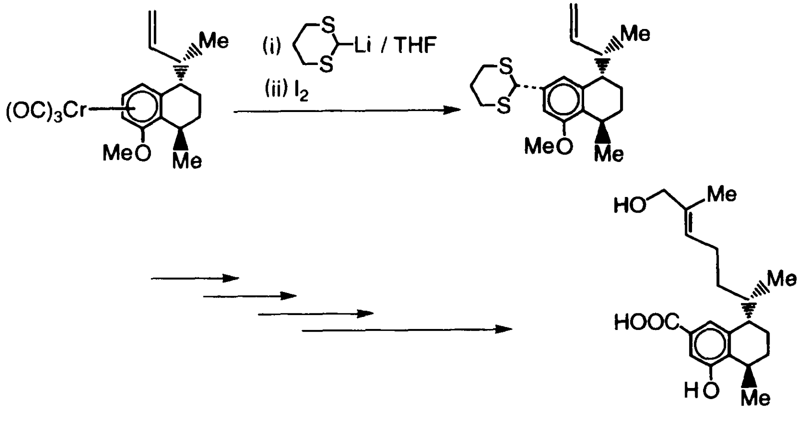
Acorenone

synthesis of the intermediate of dihydroxyserrulatic acid of antiinflammatory and analgesic as shown in eq. (13.34), the meta-directing property of methoxy group on benzene ring is used. The selectivity of this direction is very high, the other isomers are not detected [62,63].

The meta-directing property of η^6-(arene)Cr(CO)$_3$ is also used for the syntheses of steroid hormones [64,65], frenolicin of natural quinone type antibiotics [66], etc. The reactions using η^6-(arene)Cr(CO)$_3$ with high stereospecificity proceed because the aromatic ring is coordinated by the bulky Cr(CO)$_3$ group as shown in Figure 13.3. For example, methylation proceeds from the opposite side from where the benzene ring is coordinated to the chromium and a single product is yielded as shown in eq. (13.35) [67].

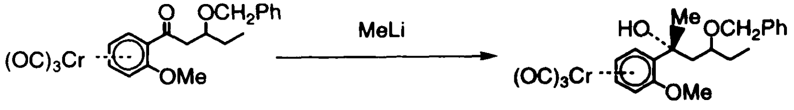
The racemic chromium compounds of ortho-substituted benzylalcohol react with isopropenylacetate in the presence of a lipase, the acylation proceeds only on the opposite side to the chromium metal as shown in eq. (13.36) [68].

The hydrogens of the aromatic ring and the hydrogens of the substituted alkyl group have a strong acidity since the aromatic ring bonds to three electron-with-



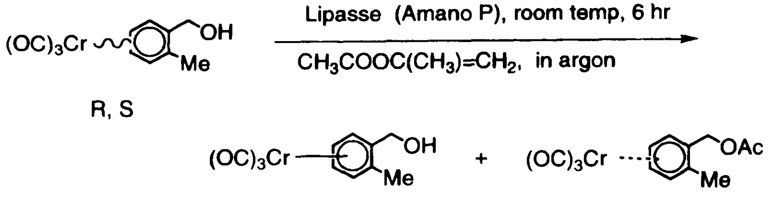
(13.34)

Dihydroxyserrulatic acid



(13.35)

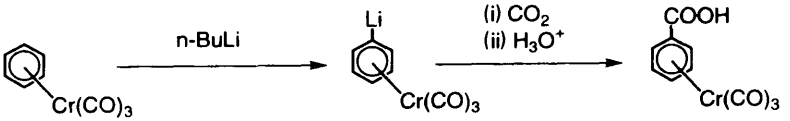
mp 110°C



(13.36)

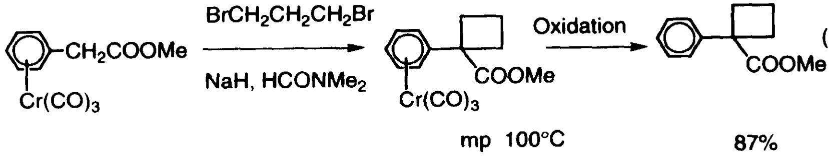
R Yield 47%, 100 ee% S Yield 48%, 98 ee%

drawing carbonyl groups in η^6-(arene)$Cr(CO)_3$, as shown in Figure 13.3. In particular, lithiation is liable to proceed with alkyllithium as shown in eq. (13.29), for example, η^6-$(C_6H_6)Cr(CO)_3$ reacts with *n*-BuLi between −45 °C and −40 °C in THF, followed by a reaction with carbon dioxide to afford carboxylic acids as shown in eq. (13.37). But, under the same reaction conditions, benzene which is not coordinated with the $Cr(CO)_3$ group does not react with *n*-BuLi [58].



(13.37)

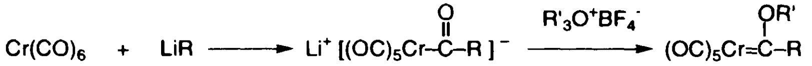
In the aromatic ring which is coordinated by $Cr(CO)_3$, not only the hydrogens of the aromatic ring have acidity but also the hydrogens of the substituted groups have acidity. For example, in hydrogen at the α-position of the alkoxycarbonylalkyl group, the dialkylation reaction easily proceeds at room temperature with alkyl halides, but the alkylation of $PhCH_2COOMe$ which is not coordinated with the $Cr(CO)_3$ group, does not proceed as shown in eq. (13.38) [69].



(13.38)

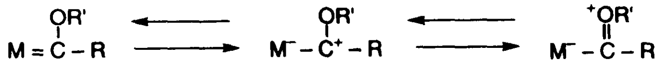
13.5.2 CARBENE REACTIONS

Organochromium compounds are able to easily form stable carbene complexes as described in the above section [70–75]. The representative method is as follows: hexacarbonylchromium reacts with a nucleophile to give an acylanion, then the chromium carbene is prepared by alkylation of the acyloxygen with a trialkyloxonium salt or a diazomethane as shown in eq. (13.39). As this reaction was



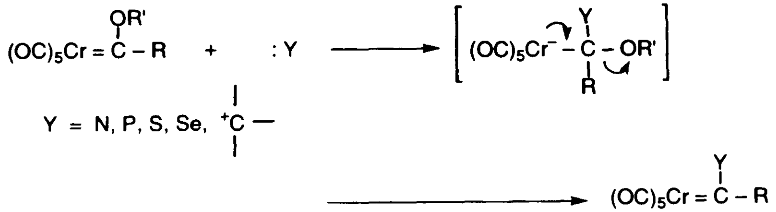
$$Cr(CO)_6 + LiR \longrightarrow Li^+[(OC)_5Cr-\overset{\overset{\Large O}{\|}}{C}-R]^- \xrightarrow{R'_3O^+BF_4^-} (OC)_5Cr{=}\overset{\overset{OR'}{|}}{C}-R \quad (13.39)$$

found in 1964 by Fisher, the $(OC)_5Cr=CR(OR')$ is named the Fisher carbene [75]. As the Fisher carbene forms the resonance structures shown in eq. (13.40), it is



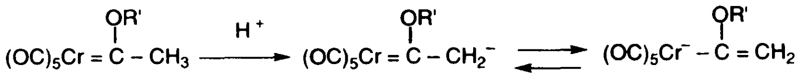
$$M=\overset{\overset{OR'}{|}}{C}-R \rightleftarrows M^--\overset{\overset{OR'}{|}}{C^+}-R \rightleftarrows M^--\overset{\overset{^+OR'}{\|}}{C}-R \quad (13.40)$$

liable to be attacked by a nucleophile. If the carbene reacts with the nucleophile, the nucleophile attacks the carbene carbon atom, simultaneously eliminating alkoxy group, and seemingly a substitution reaction proceeds as shown in eq. (13.41). The carbene carbon is liable to yield δ^+ with resonance structure shown in eq. (13.40), and the hydrogen at the α-position is liable to be drawn out by a base as shown in eq. (13.42) [76]. For example, chromium carbene reacts with *n*-BuLi, then reacts with an electrophile to afford the substituted carbene complex, and metal is eliminated by the reaction of oxidizing agent such as Ce(IV), oxygen and pyridine N-oxide to afford an ester as shown in eq. (13.43) [76].

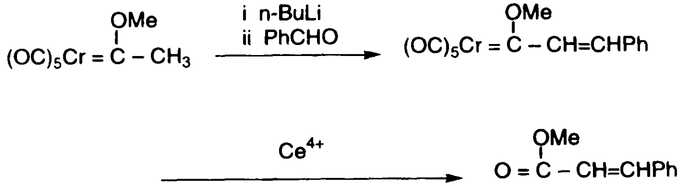


$$(OC)_5Cr{=}\overset{OR'}{C}{-}R + :Y \longrightarrow \left[(OC)_5Cr^{-}{-}\underset{R}{\overset{Y}{C}}{-}OR'\right] \longrightarrow (OC)_5Cr{=}\overset{Y}{C}{-}R \qquad (13.41)$$

Y = N, P, S, Se, $^{+}C{-}$

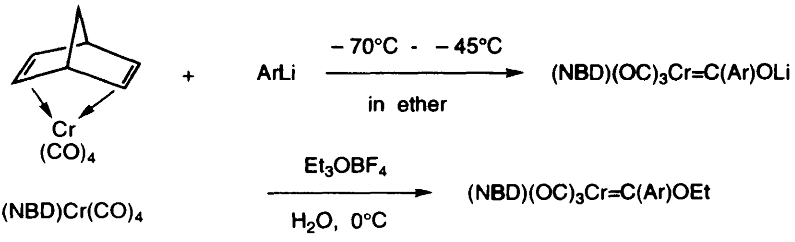


$$(OC)_5Cr{=}\overset{OR'}{C}{-}CH_3 \xrightarrow{H^+} (OC)_5Cr{=}\overset{OR'}{C}{-}CH_2^{-} \rightleftarrows (OC)_5Cr^{-}{-}\overset{OR'}{C}{=}CH_2 \qquad (13.42)$$



$$(OC)_5Cr{=}\overset{OMe}{C}{-}CH_3 \xrightarrow[\text{ii PhCHO}]{\text{i n-BuLi}} (OC)_5Cr{=}\overset{OMe}{C}{-}CH{=}CHPh \xrightarrow{Ce^{4+}} O{=}\overset{OMe}{C}{-}CH{=}CHPh \qquad (13.43)$$

Norbornadienetetracarbonylchromium, in the same manner as the Fisher carbene synthesis, reacts with organolithium compounds to afford an acyl derivative by attacking the carbonyl group, and it changes to the carbene alcoholate and reacts with Et_3OBF_3 to produce the alkyl derivative as shown in eq. (13.44) [77]. The bond length of Cr$=$C is 1.942 Å and it is shorter than that of Cr$=$C in



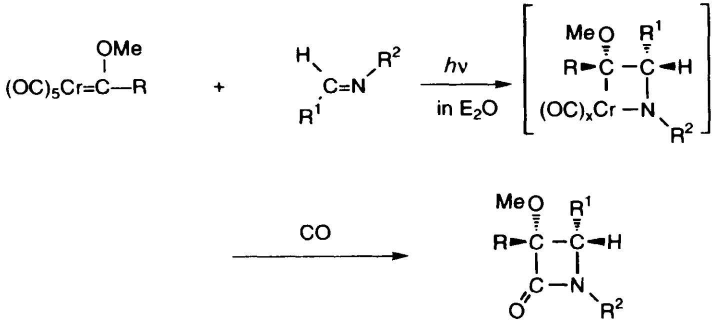
$$(NBD)Cr(CO)_4 + ArLi \xrightarrow[\text{in ether}]{-70°C\ -\ -45°C} (NBD)(OC)_3Cr{=}C(Ar)OLi \xrightarrow[H_2O,\ 0°C]{Et_3OBF_4} (NBD)(OC)_3Cr{=}C(Ar)OEt \qquad (13.44)$$

Ar = Ph, o-Me-C_6H_4, m-Me-C_6H_4, p-Me-C_6H_4,
p-MeO-C_6H_4, p-CF_3-C_6H_4

Cr=C : 1.942 Å (Ar = p-Me-C_6H_4)

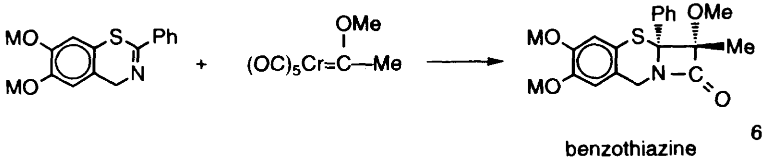
$(OC)_5Cr{=}C(Ph)OMe$ ($Cr{=}C$: 2.04 Å) obtained from hexacarbonylchromium [77].

The Fisher carbenes react with imines under the irradiation of visible light to stereoselectively afford the β-lactam, and this reaction is available for synthesis of penicillin analogues as shown in eq. (13.45). For example, benzothiazine is synthesized in a high yield by a reaction with cyclic imines as shown in eq. (13.46) [78].



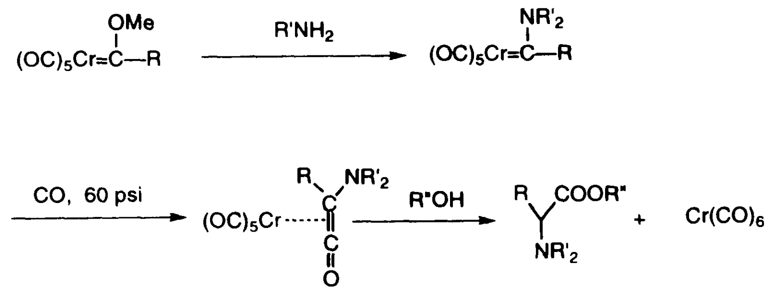
(13.45)

R, R^1, R^2 = Me, Ph
Yield = 52% - 76%

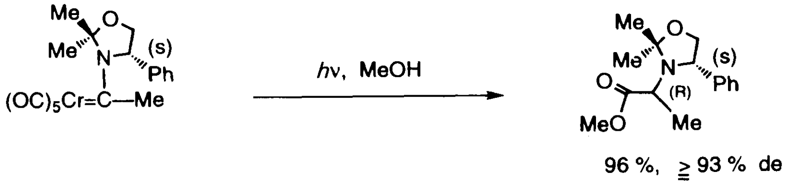


(13.46)

Fisher carbenes easily react with an amine to give the aminocarbene, and the aminocarbene reacts with carbon monoxide under light irradiation to give an aminoester as shown in eq. (13.47) [79]. If the optically active oxazolidine derivatives are used as the aminocarbene, by photolytic carbonylation the above synthesis of amino acid ester gives an optically active derivative as shown in eq. (13.48) [79].



(13.47)

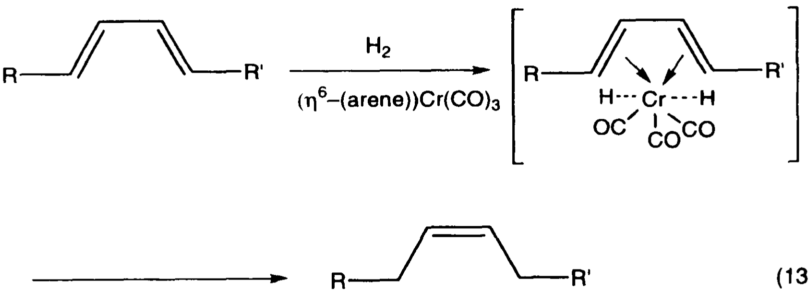


(13.48)

Recently, many organosynthesis reactions with these carbene complexes have been reported.

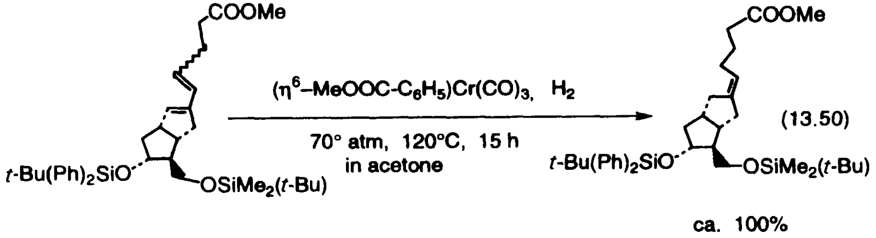
13.5.3 REDUCTION AND ISOMERIZATION

η^6-(Arene)Cr(CO)$_3$ is able to be used as the catalyst for the cis-1,4-hydrogenation of a conjugate diene, followed by the synthesis of a Z type monoene as shown in eq. (13.49). Similar reactions proceed in the presence of molybdenum and tungsten complexes as catalysts. These catalysts are more reactive than chromium catalysts but the reaction selectivities are low. The induction period is usually one hour. The induction period is thought to be caused by the ligand exchange reaction of an aryl group and diene with the obvious formation of an intermediate as shown in eq. (13.49). The activity of the catalyst is related to the Cr-C bond length and the milder reduction proceeds with the longer Cr-C bond length. For example, the reactivity of naphthalene and phenanthrene complexes are higher than that of benzene complex, and the reaction with the former catalysts proceeds at ordinary temperatures and pressures [80]. The reaction which reduces a diene to the Z type of a monoene is applied to the synthesis of a physiologically active carbacyclin intermediate. As shown in eq. (13.50), *cis* 1,4-addition is almost quantitatively prepared by using a methylbenzoate complex [80].



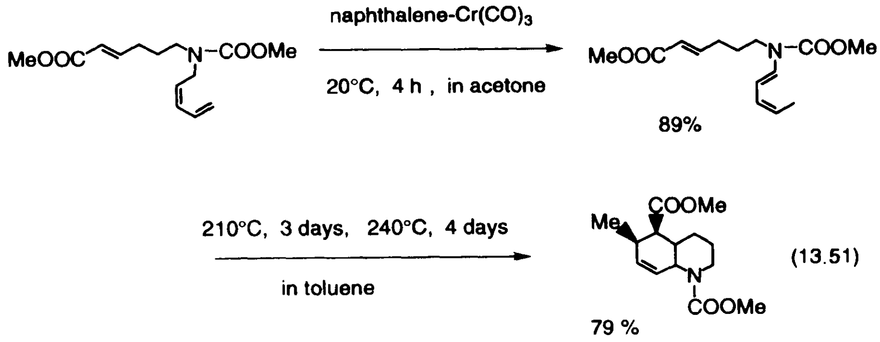
(13.49)

The reduction with η^6-(arene)Cr(CO)$_3$ proceeds by ligand exchange reaction via an intermediate as shown in eq. (13.49). If no hydrogen is present, the coordination bond of chromium metal to diene is isomerized to a more stable structure [54,81,82]. For example, the isomerization of dienamine derivatives of *cis*-octa-



(13.50)

hydroquinoline intermediate with naphthalenechromium complex affords a single product in 89% yield as shown in eq. (13.51) [81].



(13.51)

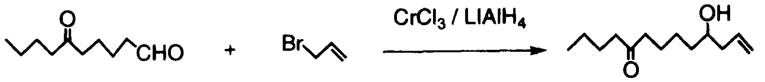
13.5.4 OTHERS

In the organosynthetic reactions with chromium, reductions with $CrCl_2$ [54,83–86] or oxidations with Cr(0), Cr(III) and Cr(IV) [87] have been reported.

$CrCl_2$ is not a strong reducing agent, but it is able to reduce active halides such as aryl halides to afford organochromium compounds. The obtained organochromium compounds, have a higher covalent bond property than organolithium compounds or organomagnesium compounds. Therefore, the nucleophilicity as a carbanion is weak, and it is able to react with a formyl group selectively without influencing to a keto carbonyl or an ester carbonyl group. The synthesis of $CrCl_2$ was usually done in an aqueous solvent, but Nozaki and Hiyama [83] found that $CrCl_3/LiAlH_4$ is able to be used in an organic solvent as shown in eq. (13.52). They have widely investigated the coupling reactions between unsaturated compounds such as alkenyl, alkynyl, aryl and vinyl, and carbonyl compounds such as aldehydes or ketones with $CrCl_3/LiAlH_4$ which yield $CrCl_2$ in the reaction system. These reactions are called Nozaki–Hiyama reactions [86].

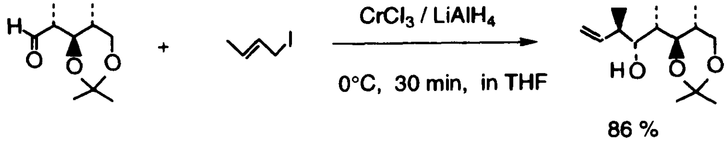
$$CrCl_3 \quad + \quad 1/2\ LiAlH_4 \xrightarrow[\text{in THF}]{0\ ^\circ\text{C}} CrCl_2 \quad + \quad H_2 \qquad (13.52)$$

The Nozaki–Hiyama reactions are able to proceed by the coupling reaction of carbonyl compounds such as ketone and aldehyde with unsaturated halides to afford selectively an aldehyde carbonyl coupling reaction product as shown in eq. (13.53) [83].



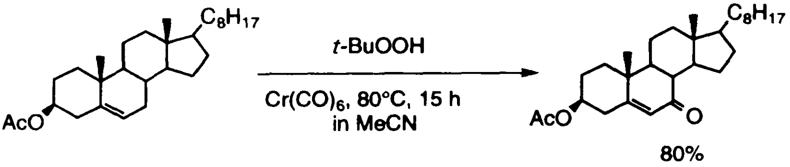
(13.53)

The Nozaki–Hiyama reactions are applied mainly to coupling reactions between aldehydes and unsaturated halides. For example, an intermediate of antibiotics rifamycin S synthesis is shown in eq. (13.54) [86,86a].



(13.54)

Chromium compounds such as $Cr(CO)_6$, $Cr(CO)_5(MeCN)$, Cr_2O_7, $Cr(acac)_3$, $Cr(OCOR)_3$ and $K_2Cr_2O_7$ are used as oxidizing agents [87]. In these compounds, $Cr(CO)_6$ is used as an organosynthetic reagent. For example, the synthesis of steroid hormone is applied to the oxidation of an allyl group to an enone as shown in eq. (13.55) [54,87–90].



(13.55)

REFERENCES

[1] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.

[2] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol. A7, p. 43, 1990.

[3] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., John Wiley, New York, vol. 6, p. 54, 1980.

[4] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 4th ed., John Wiley, New York, vol. 6, p. 228, 1993.

[5] *12093 no Kagaku Shohin*, Kagaku Kogyo Nipposha, p. 87, 1993.

[6] *Kagaku Binran Ooyohen*, Japan Chemical Society, Maruzen, Tokyo, p. 314, 1980.

[7] W.E. Silverthorn, *Adv. Organomet. Chem.*, **13** (1975) 47.

[8] R. Davis and L.A.P. Kane-Maguire, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 3, p. 953, 1982.

[9] F. Hein, *Chem. Ber.*, **52** (1919) 195.

[10] H.H. Zeiss and M. Tsutsui, *126th Meeting Amer. Chem. Soc. Abstr.* p. 29-0, 1954.

[11] H.H. Zeiss, P.J. Wheatley and H.J.S. Winkler, *Benzenoid-Metal Complexes*, Ronald Press, New York, 1966.

[12] J. Hähle and G. Stolze, *Z. Naturforsch., B*, **19** (1964) 1081.

[13] R.P.A. Sneeden, *Organochromium Compounds*, Academic Press, New York, 1975.

[14] E.O. Fischer and W. Hafner, *Z. Naturforsch., B*, **10** (1955) 665.

[15] *Shinjikken Kagaku Kouza 12, Yuki Kinzoku Kagaku*, Maruzen, Tokyo, p. 107, 1976.

[16] G. Huttner and E.O. Fischer, *J. Organomet. Chem.*, **3** (1965) 330.

[17] M. Tsutsui and G. Chang, *Can. J. Chem.*, **41** (1963) 1255.

[18] M. Tsutsui and M.N. Levy, *J. Chem. Soc. Chem. Commun.*, (1963) 117.

[19] P.L. Timms, *J. Chem. Soc. Chem. Commun.*, (1969) 1033.

[20] P.L. Timms, *J. Chem. Educ.*, **49** (1972) 782.

[21] K.J. Klabunde, *Acc. Chem. Res.*, **8** (1975) 393.

[22] P.S. Skell, D.L. Williams-Smith and M.J. McGlinchey, *J. Am. Chem. Soc.*, **95** (1973) 3337.

[23] C. Elschenbroich and R. Möckel, *Angew. Chem.*, **89** (1977) 908.

[24] W.M. Lamanna, *J. Am. Chem. Soc.*, **108** (1986) 2096.

[25] C. Elschenbroich, R. Möckel and U. Zenneck, *Angew. Chem. Int. Ed. Engl.*, **17** (1978) 531.

[26] I. Omae, *Organometallic Intramolecular-coordination Compounds*, *J. Organomet. Chem. Library 18*, Elsevier, Amsterdam, 1986.

[27] C. Elschenbroich and A. Salzer, *Organometallics*, VCH, Weinheim, 1989.

[28] M. Yoshifuji, *Yuki Gosei Kagaku Kyokaishi*, **37** (1979) 1034.

[29] S.W. Kirtley, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 3, p. 783, 1982.

[29a] J.K. Shen, J.W. Freeman, N.C. Hallinan, A.L. Rheingold, A.M. Arif, R.D. Ernst and F. Basolo, *Organometallics*, **11** (1992) 3215.

[29b] F. Cohen, R. Goumont, H. Rudler, J.C. Daran and R.A. Toscano, *J. Organomet. Chem.*, **431** (1992) C6.

[30] J.D. Munro and P.L. Pauson, *J. Chem. Soc.*, (1961) 3475.

[31] B. Nicholls and M.C. Whiting, *J. Chem. Soc.*, (1959) 551.

[32] G.K.-I. Magomedov, *J. Organomet. Chem.*, **385** (1990) 113.

[33] H.E. Podall, J.H. Dunn and H. Shapiro, *J. Am. Chem. Soc.*, **82** (1960) 1325.

[34] W. Strohmeier, *Chem. Ber.*, **94** (1961) 2490.

[35] G. Bähr and D.-C.H. Zohm, *Angew. Chem.*, **75** (1963) 94.

[36] L.E. Manzer, *J. Organomet. Chem.*, **135** (1977) C6.

[37] H.H. Zeiss and W. Herwig, *J. Am. Chem. Soc.*, **80** (1958) 2913.

[38] W. Herwig, W. Metlesics and H. Zeiss, *J. Am. Chem. Soc.*, **81** (1959) 6203.

[39] M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, **82** (1960) 6255.

[40] P.S. Skell, D.L. Williams-Smith and M.J. McGlinchey, *J. Am. Chem. Soc.*, **95** (1973) 3337.

[41] F. Jellinek, *Nature*, **187** (1960) 871.

[42] F. Jellinek, *J. Organomet. Chem.*, **1** (1963) 43.

[43] F.A. Cotton, W.A. Dollase and J.S. Wood, *J. Am. Chem. Soc.*, **85** (1963) 1543.

[44] J.A. Ibers, *J. Chem. Phys.*, **40** (1964) 3129.

[45] E. Weiss and E.O. Fischer, *Z. Anorg. Allg. Chem.*, **286** (1956) 142.

[46] E. Keulen and F. Jellinek, *J. Organomet. Chem.*, **5** (1966) 490.

[47] E. Förster, G. Albrecht, W. Dürselen and E. Kurras, *J. Organomet. Chem.*, **19** (1969) 215.

[48] B. Ress and P. Coppens, *Acta Cryst.*, **B29** (1973) 2515.
[49] A.D. Hunter, L. Shilliday, W.S. Furey and M.J. Zaworotko, *Organometallics*, **11** (1992) 1550.
[50] J. Li, A.D. Hunter, R. McDonald, B.D. Santarsiero, S.G. Bott and J.L. Atwood, *Organometallics*, **11** (1992) 3050.
[51] W.M. Lamanna, W.B. Gleason and D. Britton, *Organometallics*, **6** (1987) 1583.
[52] H. Wadepohl, *Angew. Chem. Int. Ed. Engl.*, **31** (1992) 247.
[52a] F.A. Cotton and D.C. Richardson, *Inorg. Chem.*, **11** (1966) 1851.
[53] O.S. Mills, *Pure Appl. Chem.*, **20** (1969) 117.
[53a] A.C. Filippou, K. Wanninger and C. Mehnert, *J. Organomet. Chem.*, **461** (1993) 99.
[53b] J.A. Acho and S.J. Lippard, *Organometallics*, **13** (1994) 1294.
[53c] C. Elschenbroich, J. Schneider, H. Prinzbach and W.-D. Fessner, *Organometallics*, **5** (1986) 2091.
[53d] C. Elschenbroich, T. Isenburg, B. Metz, A. Behrendt and K. Harms, *J. Organomet. Chem.*, **481** (1994) 153.
[54] J. Tsuji, *Yukigosei okaeta Sen-i-kinzoku*, Kagakudojin, Kyoto, 1991.
[55] M.F. Semmelhack, G.R. Clark, J.L. Garcia, J.J. Harrison, Y. Thebtaranonth, W. Wulff and A. Yamashita, *Tetrahedron*, **37** (1981) 3957.
[56] P.J. Dickens, J.P. Gilday, J.T. Negri and D.A. Widdowson, *Pure Appl. Chem.*, **62** (1990) 575.
[57] E.P. Kündig, (translator: M. Uemura), *Kagaku Zokan*, **105** (1985) 175.
[58] M. Yoshifuji, *Kagaku no Ryoiki*, **32** (1978) 98.
[58a] M. Sodeoka and M. Shibasaki, *Synthesis*, (1993) 643.
[58b] M. Uemura, *Yuki Gosei Kagaku Kyokaishi*, **51** (1993) 754.
[59] M.F. Semmelhack, H.T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu and J. Clardy, *J. Am. Chem. Soc.*, **101** (1979) 3535.
[60] M.F. Semmelhack, G.R. Clark, R. Farina and M. Saeman, *J. Am. Chem. Soc.*, **101** (1979) 217.
[61] M.F. Semmelhack and A. Yamashita, *J. Am. Chem. Soc.*, **102** (1980) 5926.
[62] M. Uemura, H. Nishimura and Y. Hayashi, *Tetrahedron Lett.*, (1990) 2319.
[63] M. Uemura, H. Nishimura, T. Minami and Y. Hayashi, *J. Am. Chem. Soc.*, **113** (1991) 5402.
[64] G. Jaouen, *Pure Appl. Chem.*, **58** (1986) 597.
[65] H. Künzer and M. Thiel, *Tetrahedron Lett.*, (1988) 3223.
[66] M.F. Semmelhack and A. Zask, *J. Am. Chem. Soc.*, **105** (1983) 2034.
[67] M. Uemura, T. Minami and Y. Hayashi, *J. Am. Chem. Soc.*, **109** (1987) 5277.
[68] K. Nakamura, K. Ishihara, A. Ohno, M. Uemura, H. Nishimura and Y. Hayashi, *Tetrahedron Lett.*, (1990) 3603.
[69] G. Jaouen, A. Meyer and G. Simonneaux, *J. Chem. Soc. Chem. Commun.*, (1975) 813.
[70] E.O. Fischer and A. Maasböl, *Angew. Chem. Int. Ed. Engl.*, **3** (1964) 580.
[71] E.O. Fischer, C.G. Kreiter, H.J. Kollmeier, J. Müller and R.D. Fischer, *J. Organomet. Chem.*, **328** (1971) 237.
[72] E.O. Fischer, H. Hollfelder, F.R. Kreissl and W. Uedelhoven, *J. Organomet. Chem.*, **113** (1976) C31.
[73] D.J. Cardin, B. Cetinkaya and M.F. Lappert, *Chem. Rev.*, **72** (1972) 545.
[74] D.J. Cardin, B. Centinkaya, M.J. Doyle and M.F. Lappert, *Chem. Soc. Rev.*, **2** (1973) 99.
[75] A. Yamamoto, *Yuki Kinzoku Kagaku, Kiso to Ooyo*, Shokabo, 1982.
[76] Y. Yamamoto and Y. Naruta, *Yuki Kinzoku Kagaku*, Maruzen, p. 207, 1983.
[77] J. Chen and B. Wang, *J. Organomet. Chem.*, **440** (1992) 67.
[78] L.S. Hegedus, *Pure Appl. Chem.*, **55** (1983) 1745.
[79] L.S. Hegedus, *Pure Appl. Chem.*, **62** (1990) 691.
[80] M. Shibasaki and M. Sodeoka, *Yuki Gosei Kagaku Kyokaishi*, **43** (1985) 877.

[81] H. Yamada, M. Sodeoka and M. Shibasaki, *J. Org. Chem.*, **56** (1991) 4569.
[82] M. Sodeoka, H. Yamada and M. Shibasaki, *J. Am. Chem. Soc.*, **112** (1990) 4906.
[83] T. Hiyama, *Yuki Gosei Kagaku Kyokaishi*, **39** (1981) 81.
[84] K. Takai and K. Utimoto, *Yuki Gosei Kagaku Kyokaishi*, **46** (1988) 66.
[85] K. Utimoto and K. Takai, *Yuki Gosei Kagaku Kyokaishi*, **48** (1990) 962.
[86] P. Cintas, *Synthesis*, (1992) 248.
[86a] H. Nagaoka and Y. Kishi, *Tetrahedron*, **37** (1981) 3873.
[87] J. Muzart, *Chem. Rev.*, **92** (1992) 113.
[88] A.J. Pearson, Y.-S. Chen, S.-Y. Hsu and T. Ray, *Tetrahedron Lett.*, (1984) 1235.
[89] A.J. Pearson, Y.-S. Chen, G.R. Han, S.-Y. Hsu and T. Ray, *J. Chem. Soc., Perkin Trans.* **1**, (1985) 267.
[90] A.J. Pearson and G.R. Han, *J. Org. Chem.*, **50** (1985) 2791.

14 Organomanganese Compounds

14.1 INTRODUCTION

Manganese is a well known element, being one component of the alloys, MnO_2 for a dry battery and for an oxidizing agent, $KMnO_4$; however, organomanganese compounds are generally not well known compounds. This chapter shows the preparation, structure and reactions, etc. of organomanganese compounds.

14.2 MANGANESE

Manganese is a transition metal of group 7 of the periodic table and the outer electron shell is $3d^5 4s^2$. Manganese is present at 950 ppm in the Earth's crust [1], and is the next most abundant transition element after iron and titanium.

Manganese amounts to about 15 mg in the living body, especially in internal organs, hair and bone [2–3a].

Deep-sea manganese nodules at depths of 4–6 km is a manganese ore which grew on a nucleus of very small pieces of stone and shark teeth by 1–10 mm/10^6 y. Mn (1.3–35%) and Fe (4.8–42%) are the main components and the others are Ni, Cu and Co. Several multinational private consortia were formed in the 1970s to explore and develop the mining and extraction processes for deep-sea nodules. In the mid-1990s, however, none have a short-term development plan. It is a potentially important future source of manganese [2–3a].

The major ore of manganese is pyrolusite [4–7]. If manganese ores are not soluble in an acid, they are reductively roasted at 700 °C to produce manganese oxide (MnO), and manganese is removed with sulfuric acid. Fe, Al, Mo, As and Si as impurities are removed from solution by neutralization. As a small amount of As, Cu, Pb, Ni and Co are contained in the neutralized solution still, these are removed as their sulfate by adding H_2S and 99.97% pure manganese is prepared by the electrolysis of the solution as the electrolyte [4–7].

Manganese is a silver-gray metal, resembling iron, and is hard and very brittle. Manganese is more electrically positive than iron and is oxidized on its surface in air with a brown protective coating being formed. Powdered manganese ignites sometimes by heating and manganese is easily dissolved in dilute acid to form a Mn(II) salt. It reacts with sodium carbonate or potassium carbonate. Manganese reacts with water or steam with liberation of hydrogen. At high temperatures it reacts with oxygen, nitrogen, chlorine and fluorine to yield Mn_3O_4, Mn_3N_2, $MnCl_2$ and $MnF_2 + MnF_3$. It reacts directly with boron, carbon, phosphorus and sulfur [2,3,6–9].

Manganese exists in four allotropic forms: α, β, γ, and δ. The transition temperatures are 727 °C, 1095 °C, 1104 °C and 1244 °C, and the δ-form changes to liquid at 1244 °C.

The properties of the α-form are shown in Table 14.1. Manganese is of little use alone: it is mainly used by being added to metals such as iron, copper, nickel and aluminum as an alloying agent to improve strength, toughness, hardness, abrasion resistance, ductility and processability. For example, manganese steel containing 12% of manganese (Hadfield manganese steel) is very hard, and is used for railway points and disintegrator (crusher), etc.

The most important uses of manganese are in stainless steels, special steels, and a deoxidizer. The representative inorganic compound of manganese is MnO_2. MnO_2 is most used in dry batteries. The other uses are as an oxidizing agent, a coloring agent for stained glass, raw materials for matches, etc. $KMnO_4$, a strong oxidizing agent, is largely used as the raw material in pharmaceuticals and a bleaching agent, etc. Manganese chloride, manganese borate, manganese sulfate and manganese carbonate, etc. are used as desiccants and pigments, etc.

Organomanganese compounds have only been used since the end of 1930's. Organomanganese compounds are generally almost unknown as organometallic compounds besides $(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$ as an antiknock agent.

Table 14.1 Physical properties of manganese [4]

Property	Value
melting point, °C	1244
boiling point, °C	2032
crystal structure	complex cubic
density, 20 °C, g/cm^3	7.44
standard electrode potential, V	1.134
specific heat at 25 °C, J g^{-1}K^{-1}	0.477
hardness, Mohs scale	5
latent heat of fusion, J/g	244
latent heat of vaporization, J/g	4020
heat of transition, J/mol	2240
coefficient of linear expansion, K^{-1}	22.3×10^{-6}
resistivity at 20 °C, Ωcm	$150–260 \times 10^{-6}$
enthalpy, J/mol	4999
entropy, J mol^{-1}K^{-1}	32.0
compressibility, m^2/N	8.4×10^{-7}

14.3 PREPARATION OF ORGANOMANGANESE COMPOUNDS

Organomanganese compounds are prepared by the following six processes.

(1) Reductive carbonylation
(2) Reactions with organoalkali metal compounds
(3) Reactions with organomagnesium compounds
(4) Metal vapor syntheses
(5) Reactions with organomanganese compounds
(6) Others

14.3.1 REDUCTIVE CARBONYLATION

The basic compound for the synthesis of various kinds of organomanganese compounds is dimanganese decacarbonyl ($Mn_2(CO)_{10}$). $Mn_2(CO)_{10}$ is a yellow crystal having mp 154–155 °C in a sealed tube and is soluble in a general solvent. $Mn_2(CO)_{10}$ is an 18-electron compound and is stable, and its handling is easy [10]. $Mn_2(CO)_{10}$ is prepared by the reductive carbonylation of manganese halides (or manganese acetate) with carbon monoxide and a reducing agent.

Reaction with sodiumbenzophenoneketyl as the reducing agent is shown in eq. (14.1) [11].

$$2MnCl_2 \quad + \quad 4\,Ph_2CONa \xrightarrow[\text{in THF}]{\text{(i) reflux (ii) CO, 200 atm, } 200^\circ\text{C, 2 h}} Mn_2(CO)_{10} \qquad (14.1)$$

35%

sublimation 50 - 70°C / 0.5 mm Hg

Reaction with organoaluminum compound as a reducing agent is shown in eq. (14.2) and when the molar ratio of $(CH_3COO)_2Mn$ and Et_3Al is 1 : 4, the yield is 55–60% [12].

$$(CH_3COO)_2Mn \quad + \quad Et_3Al \xrightarrow[\text{in (i-Pr)}_2\text{O}]{\text{CO, 3000 psi, } 100^\circ\text{C, 3 h}} Mn_2(CO)_{10} \qquad (14.2)$$

55 - 60 %

As in $(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$ used as an antiknock agent it is easily available at a low price. $Mn_2(CO)_{10}$ is prepared with sodium at ordinary pressure in 16–20% yield by carbonylation [13]. The yield is improved by 48% by reacting at 125 °C for 8 hours under 700 psi. If benzene is used in place of diglyme as the solvent, the yield decreases to 15%. Then it is thought that the diglyme, having a strong electron donating property, activates the reaction [14].

$$(\eta^5\text{-}C_5H_4Me)Mn(CO)_3 \quad + \quad Na \xrightarrow[\text{in diglyme}]{\text{CO, reflux, 5 h}} Mn_2(CO)_{10} \qquad (14.3)$$

16 - 20 %

sublimation 70 - 80°C/0.1 mm Hg
mp 153 - 154°C

14.3.2 REACTIONS WITH ORGANOALKALI METAL COMPOUNDS

The various kinds of organomanganese compounds are prepared by reaction of manganese halides with organolithium compounds or organosodium compounds. For example, $(\eta^5\text{-}C_5H_5)_2Mn$ is prepared by the reaction of $\eta^5\text{-}C_5H_5Na$ with $MnBr_2$ in THF by refluxing for two or three hours as shown in eq. (13.4). The solvent is removed under reduced pressure, and amber colored crystals are sublimated in vacuum. The crystal changes from a rhombic to a monoclinic system at 159–160 °C. The melting point is 172–173 °C and it is stable up to 350 °C. But it is reactive to oxygen and it ignites in air [15]. $(\eta^5\text{-}C_5H_5)_2Mn$ yields ferrocene by a reaction with $FeCl_2$ similar to CpNa and Cp_2Mg [10].

$$\eta^5\text{-}C_5H_5Na \quad + \quad MnBr_2 \xrightarrow[\text{in THF}]{\text{reflux , 2 - 3 h}} (\eta^5\text{-}C_5H_5)_2Mn \qquad (14.4)$$

45 %

sublimation 100 - 130°C/10^{-4}- 10^{-5} mm Hg

$$\underset{\text{rhombic}}{\text{amber crystal}} \xrightarrow[\text{159 -160°C}]{} \underset{\text{monoclinic}}{\text{pale pink crystal}}$$

mp 172 - 173°C

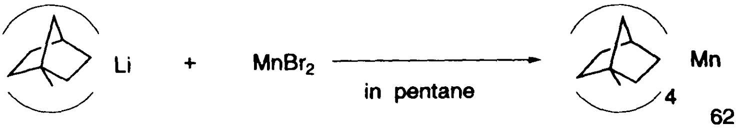
$(\eta^5\text{-}C_5Me_5)_2Mn$ is also prepared as shown in eq. (14.5), similar to the preparation method of $(\eta^5\text{-}C_5H_5)_2Mn$ (eq. (14.4)) [16]. $(\eta^5\text{-}C_5Me_5)_2Mn$ has a low reactivity compared with that of $(\eta^5\text{-}C_5H_5)_2Mn$ and it does not show an ignition property but only decomposes slowly and it does not yield a ferrocene derivative even if it reacts with $FeCl_2$ [16].

$$Z(\eta^5\text{-}C_5Me_5Li) \quad + \quad MnCl_2 \xrightarrow[\text{in THF}]{\text{40°C, 2 h}} (\eta^5\text{-}C_5Me_5)_2Mn \qquad (14.5)$$

76 %

sublimation 100°C/10^{-5} mm Hg mp 292°C

The alkyl compounds of organotransition metal compounds are difficult to synthesize because of the occurrence of β-elimination. However, cyclic compounds having bridge structures such as norbornane are relatively stable and the norbornanemanganese derivative is prepared as shown in eq. (14.6). The norbornanemanganese compound is reduced to one half at room temperature for 1 day or at 100 °C for 13.7 min [17].



(14.6)

decomp. at room temp. : 50% day

14.3.3 REACTIONS WITH ORGANOMANGNESIUM COMPOUNDS

The alkyl compounds of organotransition metal compounds, as described above, are easily decomposed by β-elimination; however, Me or Me_3SiCH_2 group which does not have a carbon at the β-position, $PhCH_2$ which does not have an alkyl-carbon at the β-position, and $CH_3C(CH_3)_2CH_2$- which does not have a hydrogen atom at the β-position afford relatively stable organomanganese compounds by reaction with Grignard reagents or with R_2Mg as shown in eq. (14.7).

$$\text{RMgX (or } R_2Mg\text{)} + MnCl_2 \longrightarrow R_2Mn \qquad (14.7)$$

R : Me, $MeC(CH_3)_2CH_2$-, $PhCH_2$-, $PhC(CH_3)_2CH_2$-, Me_3SiCH_2-
X : Cl, Br

For alkylmanganese compounds having more hydrogen atoms at the β-position, β-elimination proceeds more easily and the order of the stability of alkylmanganese compounds is as follows [17,18]:

$$n\text{-Pr},\ n\text{-Bu} > \text{Et} > t\text{-Bu}, < i\text{-Pr}$$

14.3.4 METAL VAPOR SYNTHESES

Manganese metal is able to react directly with an organic compound cooled by liquid nitrogen by evaporating the compound under vacuum. For example, reactions with aromatic compounds such as toluene, xylene and mesitylene are shown in eq. (14.8) [19–21]. In these reactions, at first, iodide complexes $(\eta^6\text{-Arene})_2Mn^+I^-$ are yielded by a reaction with iodide, and the more stable $(\eta^6\text{-Arene})_2Mn^+PF_6^-$ is isolated by reaction with NH_4PF_6 as shown in eq. (14.8) [19].

$$\underset{\text{vapor}}{\text{Mn}} + \text{Arene} \xrightarrow[]{\substack{\text{(i) } -196^\circ\text{C, } I_2\text{, 2 hr} \\ \text{(ii) room temp} \\ \text{(iii) } NH_4PF_6}} \underset{1-2\ \%}{(\eta^6\text{-Arene})_2Mn^+PF_6^-} \qquad (14.8)$$

Arene : toluene, *o*-, *m*-, *p*-xylene, mesitylene

These compounds are determined by utilizing the NMR and mass spectrographic data of $(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)Mn^+PF_6^-$ which is prepared by the reaction of Ph_2Mn with $MeC{\equiv}CMe$ and NH_4PF_6 as shown in eq. (14.9) [19,22].

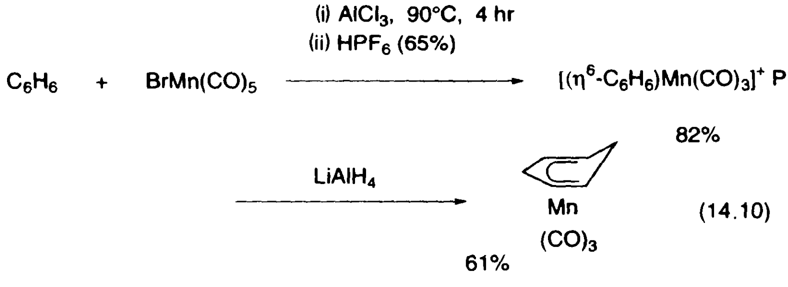
$$2\mathrm{PhMgBr} + \mathrm{MnCl_2} \xrightarrow[\text{in } n\text{-}\mathrm{Pr_2O}]{} \mathrm{Ph_2Mn}$$

$$\xrightarrow{\substack{\text{(i) } 3\,\mathrm{CH_3C{\equiv}CHCH_3} \\ \text{(ii) } \mathrm{NH_4PF_6} \\ 20^\circ - 60^\circ\mathrm{C},\ 23\,\mathrm{h}}} (\eta^6\text{-}\mathrm{C_6H_6})(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{Mn^+PF_6^-} \qquad (14.9)$$

14.3.5 REACTIONS WITH ORGANOMANGANESE COMPOUNDS

$Mn_2(CO)_{10}$ is a basic compound for the syntheses of organomanganese compounds as described above. For example, $XMn(CO)_5$, $NaMn(CO)_5$, $HMn(CO)_5$ and $MeMn(CO)_5$ are prepared from $Mn_2(CO)_{10}$ as shown in Scheme 14.1 [10,23] and these products are also used as raw materials for other organomanganese compounds.

$BrMn(CO)_5$ is prepared in 96% yield by the reaction of $Mn_2(CO)_{10}$ with bromine. The $BrMn(CO)_5$ reacts with benzene and HPF_6 to afford $[\eta^6\text{-}C_6H_7Mn(CO)_3]^+PF_6^-$ and further, by reduction with $LiAlH_4$, $\eta^5\text{-}C_6H_7Mn(CO)_3$, an 18 electron compound, is yielded [24].



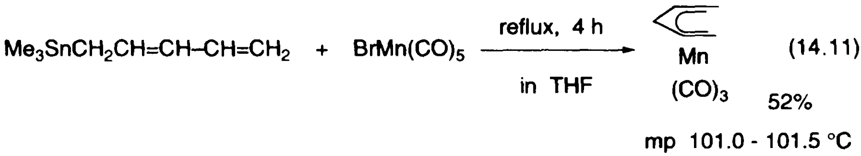
(14.10)

$$\begin{tikzcd}
\mathrm{XMn(CO)_5} & \mathrm{Mn_2(CO)_{10}} \arrow[l, "X_2"'] \arrow[r, "Na"] \arrow[d, "H_2"'] & \mathrm{NaMn(CO)_5} \arrow[d, "MeI"] \arrow[dl, "H^+"'] \\
 & \mathrm{HMn(CO)_5} \arrow[r, "CH_2H_2"] & \mathrm{MeMn(CO)_5}
\end{tikzcd}$$

X = Cl, Br, I

Scheme 14.1 [10,23].

Pentadienyl compounds similar to η^5-$C_6H_7Mn(CO)_3$ are also prepared by the reaction of pentadiene compounds of organotin compounds with manganese carbonyl compounds as shown in eq. (14.11) [25].



(14.11)

The reactions of $BrMn(CO)_5$ with allyl compounds afford the tetracarbonyl compounds for the 18-electron rule manganese atom as shown in eq. (14.12) [26].

$$CH_2{=}CH{-}CH_2Br + BrMn(CO)_5 \xrightarrow[\text{in } CH_2Cl_2]{\substack{PhCH_2NEt_3Cl,\ NaOH,\\ \text{reflux 5 hr}}} \underset{80\%}{(\eta^3\text{-}C_3H_5)Mn(CO)_4} \quad (14.12)$$

14.3.6 OTHERS

Organoaluminum compounds as arylation agents react with manganese compounds in the presence of phosphine to afford organomanganese compounds. The reaction of Mn(acac) in the presence of electron-donating phosphine which act as a stabilizer of the ligand, affords diarylphosphines in high yield as shown in eq. (14.13) [27].

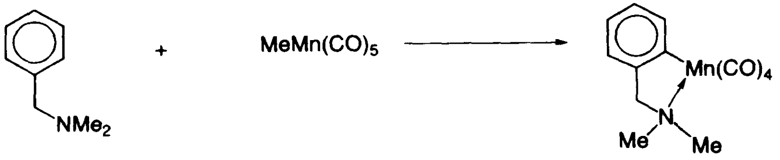
$$Mn(acac)_2 + 3AlPh_3{\bullet}Et_2O + PCy_3 \xrightarrow{-50^\circ C} \underset{\substack{93\%\\ \text{decomp. } 160-165^\circ C}}{Ph_2MnPCy_3} \quad (14.13)$$

Ph_2Mn reacts with an acetylene compound ($Me{-}C{\equiv}C{-}Me$) and the cyclotrimerized manganese complex is isolated by adding aqueous sodium tetraphenylboron as shown in eq. (14.14) [28].

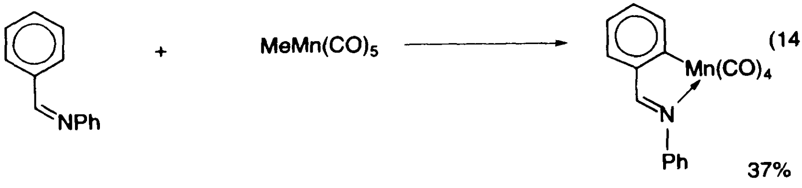
$$Ph_2Mn + CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow{\substack{\text{(i) room temp., overnight}\\ \text{(ii) } NaBPh_4}} \underset{\text{decomp. } 350^\circ C}{[(\eta^6\text{-}C_6Me_6)_2Mn]^+ BPh_4^-} \quad (14.14)$$

14.4 FIVE-MEMBERED RING COMPOUNDS

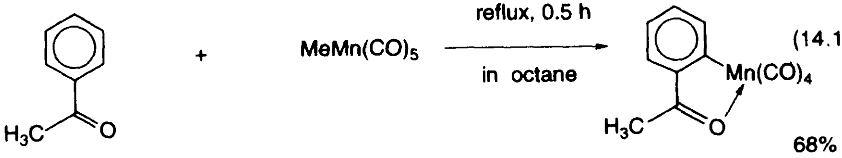
With compounds having an electron-donating atom such as N, O, S, P and As, the reactions to form a five-membered ring proceed by coordination to the metal element, and the stability of the five-membered ring is high [29]. These formation reactions of ring compounds are called cyclometalation [30] and this cyclometalation contains not only the formation of a five-membered ring, but also four-, six-, seven-, etc. membered compounds. However, only for five-membered ring can the formation reaction proceed easily and the stability of the products is high.



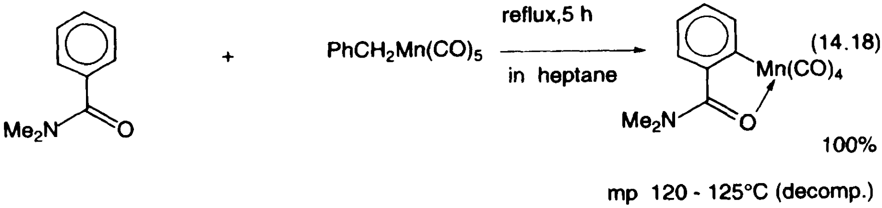
(14.15)



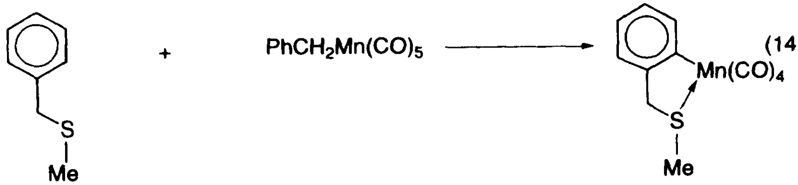
(14.16)



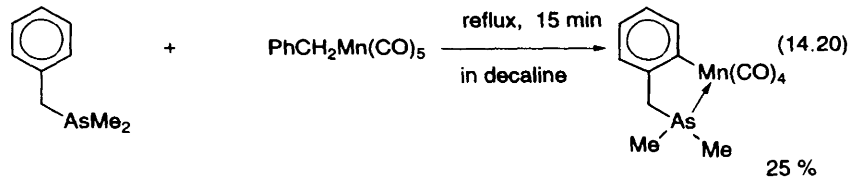
(14.17)



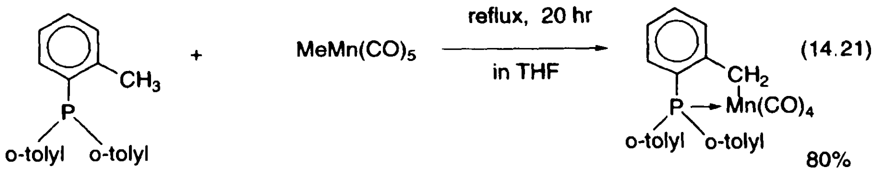
(14.18)



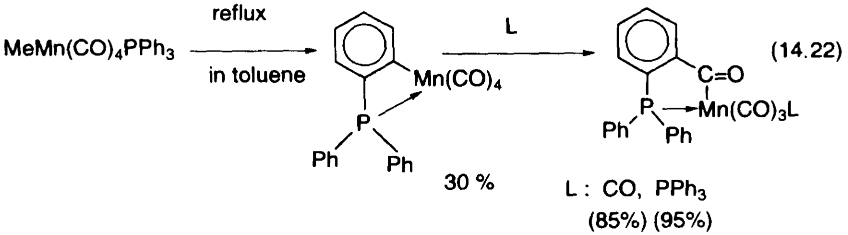
(14.19)



(14.20)



(14.21)



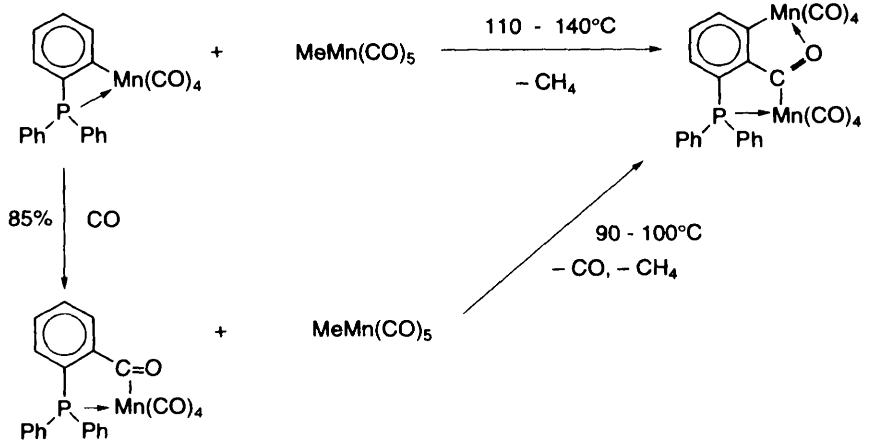
(14.22)

The cyclometalation of organomanganese compounds are shown in eqs. (14.15)–(14.22) [23a, 29–41c]. In the reaction shown in eq. (14.22) which forms a four-membered ring compound, the yield is low since many side reactions proceed. And in reaction with carbon monoxide or phosphine, the carbonyl insertion is liable to proceed to form the five-membered ring compounds. Further reaction with $MeMn(CO)_5$ or reaction of the four-membered ring compound with $MeMn(CO)_5$ forms two five-membered ring compounds as shown in Scheme 14.2 [42,43]. The many investigations into five-membered organomanganese ring compounds have been reported [10,44–54].

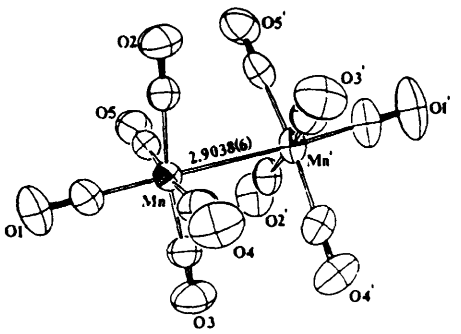
14.5 STRUCTURES OF ORGANOMANGANESE COMPOUNDS

Organomanganese compounds form mainly six-coordination structures, and few others form five- and four-coordination structures.

The structure of the basic organomanganese compounds ($Mn_2(CO)_{10}$) is shown in Figure 14.1 [55–57]. It forms a six-coordination D_{4d} symmetry structure in which Mn bonds to another Mn. The axial Mn–C bond is slightly shorter compared with the equatorial Mn–C [56].



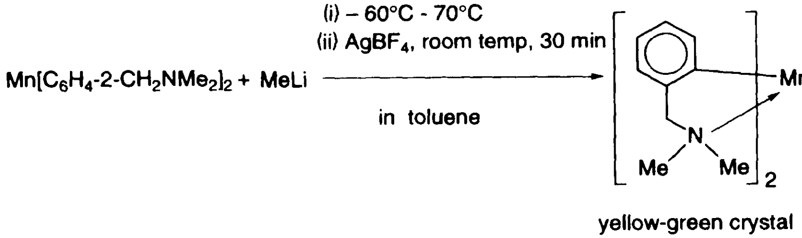
Scheme 14.2 [42,43].



axial Mn - C = 1.811 Å
average equatorial Mn - C = 1.856 Å
Mn - Mn = 2.904 Å

Figure 14.1 Geometry of the $Mn_2(CO)_{10}$ molecule [55].

Bis(2-N,N-dimethylaminomethylphenyl)manganese reacts with MeLi at low temperatures to afford a yellow-green crystal as shown in eq. (14.23). The crystal forms a trigonal bipyramidal structure and two N's, Mn and a methylcarbon form a planar structure as shown in Figure 14.2 [56].



(14.23)

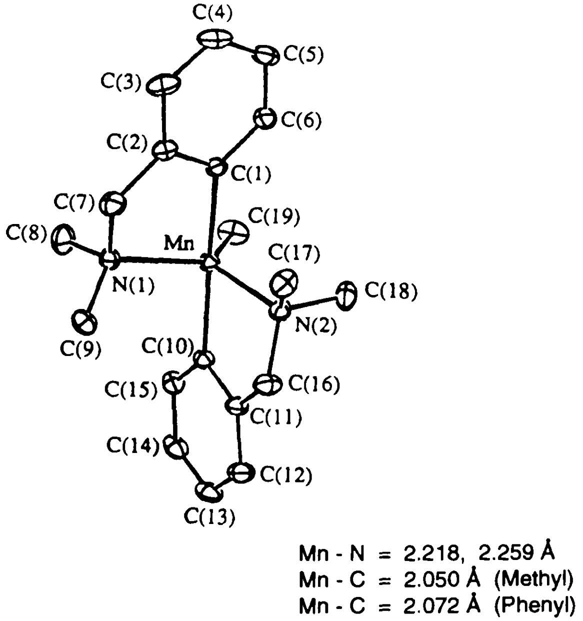


Figure 14.2 Molecular structure of $\mathrm{MeMn(2\text{-}C_6H_4\text{-}CH_2NMe_2)_2}$ [58].

$\mathrm{(Me_3SiCH_2)_2Mn}$ shown in eq. (14.24), which does not have a β-carbon, is a stable compound. The structure is shown in Figure 14.3 [59]. The one carbon bonds to two manganese atoms, namely, the compound forms a polymeric bridged structure $\mathrm{(Me_3SiCH_2)_2Mn}$, which is the most stable compound of the alkylmanganese compounds and it sublimates at 150 °C [59].

$$\underset{\text{or } \mathrm{2Me_3SiCH_2MgCl}}{\mathrm{(Me_3SiCH_2)_2Mg}} \quad + \quad \mathrm{MnCl_2} \xrightarrow{\text{room temp, 3 - 4 h}} \underset{\text{mp 150°C}}{\mathrm{(Me_3SiCH_2)_2Mn}} \qquad (14.24)$$

Mn requires eleven electrons from the ligands so as to have 18 electrons since its outer electron configuration is $3d^5 4s^2$. For example, in manganese bonded with two benzene rings in $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)Mn^+]PF_4^-$, it binds with one electron too many. Therefore manganese becomes Mn^+ by the removal of one electron from Mn. But, by reduction with $LiAlH_4$ as shown in eq. (14.25), one of the benzene rings is hydrogenated to afford $(\eta^5\text{-}C_6H_7)(\eta^6\text{-}C_6Me_6)Mn$ which then has 18 electrons [23].

On the $(\eta^6\text{-}C_6H_5Me)_2Mn^+I^-$, it is found that it has a sandwich structure like ferrocene as shown in Figure 14.4. Two benzene rings overlap one another, that is, it is an eclipsed conformation [60].

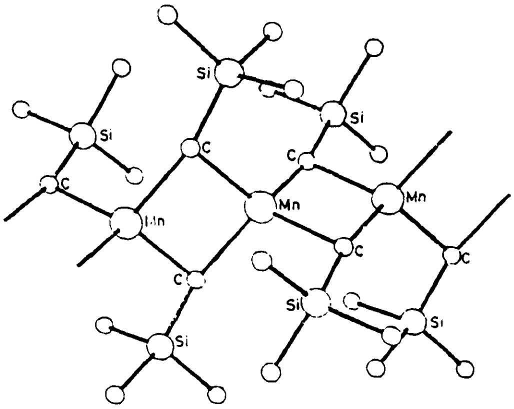
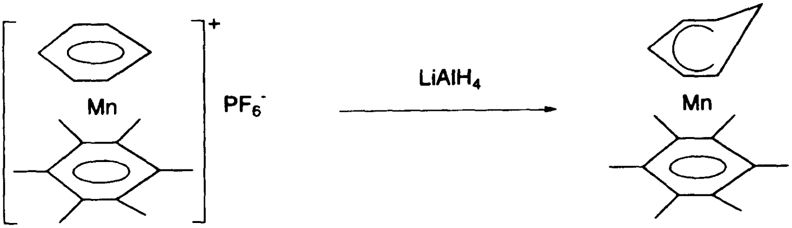
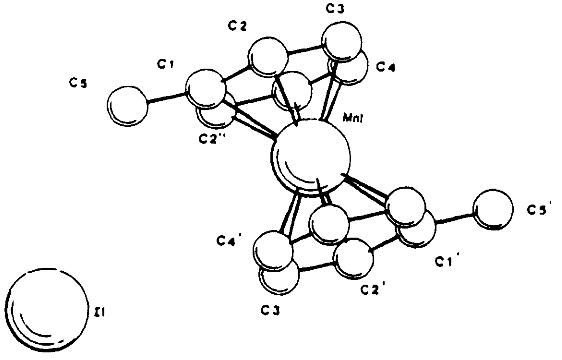


Figure 14.3 Structure of bis(trimethylsilylmethyl)manganese [59].



(14.25)

In (η^5-$C_5Me_5)_2Mn$, two cyclopentadienyl rings are in parallel, and it forms a staggered conformation as shown in Figure 14.5. This manganocene has a D_{5d} symmetry, and orbital degeneracy. This degeneracy is relieved in the solid state by the distortion of Cp rings and a small slippage of the top and bottom halves of the



C - C (C_6-ring mean) = 1.46 Å
Mn - C(C_6-ring centroid) = 1.56 Å

Figure 14.4 Molecular structure of $[\eta^6$-$C_6H_5Me]^+I^-$ [60]

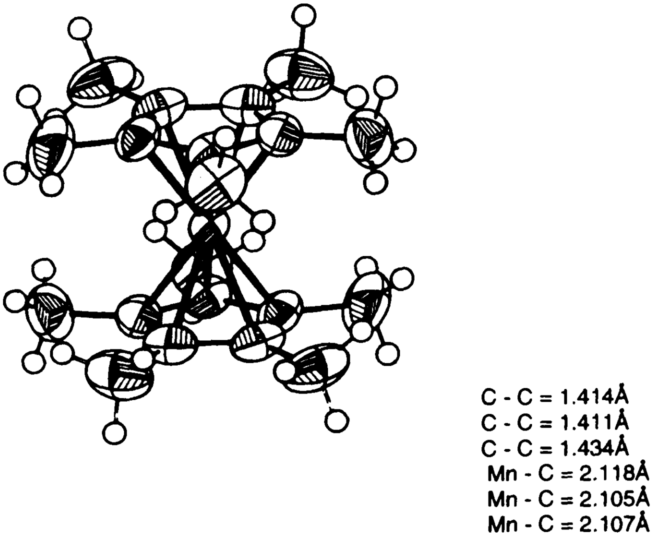


Figure 14.5 Molecular structure of (η^5-C_5Me_5)$_2$Mn [61].

metallocene sandwich. In manganocene the symmetry is out of shape due to Jahn–Teller distortion. The Cp ring is distorted with C–C bond distances ranging from 1.409 Å to 1.434 Å. This is the first example which Jahn–Teller distortion† is found in organometallic compounds [61].

The outer electron structure of chromium (see Chapter 13) is $3d^5 4s^1$ and (η^6-C_6H_6)$_2$Cr has 18 electrons and the outer electron of iron (see Chapter 15) is $3d^6 4s^2$ and (η^5-C_5H_5)$_2$Fe has 18 electrons. However, since the outer electron configuration of manganese is $3d^5 4s^2$ as described above (η^5-C_5H_5)(η^6-C_6H_6)Mn is 18 electrons. In 1966 (η^5-C_5H_5)(η^6-C_6H_6)Mn was synthesized [61a] and in 1994 it is determined that it forms a sandwich structure like chromocene and ferrocene by X-ray diffraction studies [61b,61c]. (η^5-C_5H_5)(η^6-C_6H_6)Mn decomposes at 191–192 °C in a sealed tube and it is stable in air like chromocene.

The many carbenes of organomanganese compounds have been reported [62–68b]. For example, CpMn(CO)$_3$ reacts with PhC≡CH under light irradiation to give acetylene π-complex and the carbene complex Cp(OC)$_2$Mn=C=CHPh via rearrangement as shown in eq. (14.26) [62]. In this reaction, a carbon-bridged product is also formed, and this bridged compound is also obtained by the reaction of the carbene product with CpMn(CO)$_3$ as raw material [62].

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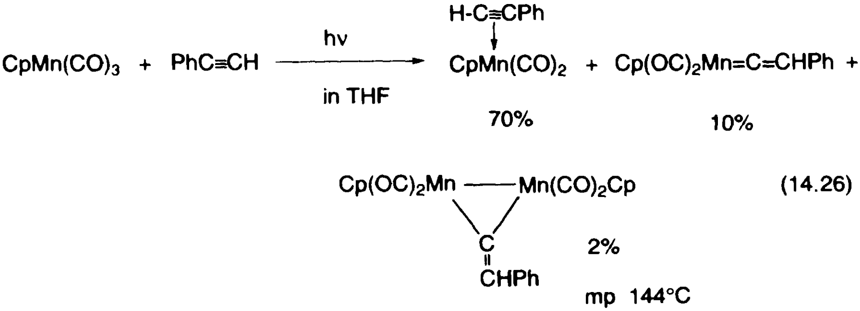
† When a nonlinear multi-atom molecule has three or more symmetry axis, molecular orbital is occasionally degenerated. If the nuclear arrangement of molecule is deformed in total to asymmetry, the degeneration is relieved and one state of them becomes with lower energy and more stable than that of high symmetric state, namely the distorted or that of low symmetric state shows a lower energy, and such a distortion is Jahn–Teller distortion.



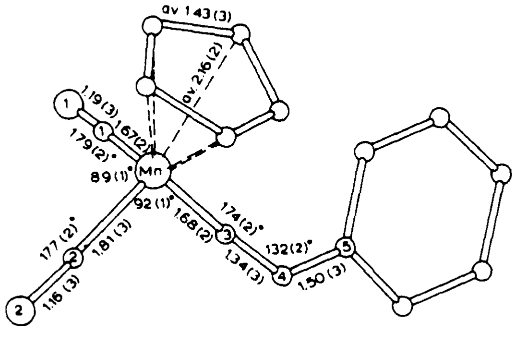
(14.26)

The structure of the carbene is shown in Figure 14.6 [63]. Mn–C bond lengths in Mn–CH_3 or Mn–aryl, as shown in Figure 14.2, are 2.050 Å or 2.072 Å and the M–C bond length of $Cp(OC)_2Mn = C = CHPh$ is 1.68 Å. The latter data is slightly shorter than the usual M–C single bond. As the M–C–C angle is 174°, these data show a linear metalallene system [63]. The electron-withdrawing property of the carbene ligand (C = CHPh) is stronger than that of the carbonyl group and the order of the electron-withdrawing ability of ligands is as follows [62].

$$SO_2 > CS > C{=}CHPh > AsF_3 > CO > PF_3 > PhC{\equiv}CPh > CPh_2 > PPh_3$$

Recently, manganese carbyne complexes are found [68c,68d] on $[Cp(OC)PPh_3Mn{\equiv}C(Me)C = CPh_2]BF_4{\cdot}CH_2Cl_2$, Mn–C bond length is 1.668 Å and that data is very slightly shorter than that of the above carbene data [68c]. On the other hand, on $(\eta^5\text{-}MeC_5H_4)(OC)_2Mn(Me)C{\equiv}CFe(CO)_2(\eta^5\text{-}C_5Me_5)$, the structure of acetylene π-complex has been reported [68e].

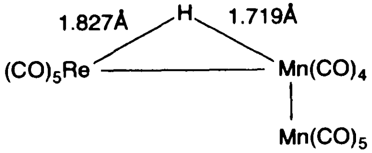
Multi-nuclear metal complexes are used as hydrogenation catalysts. The hydrogen-bridged complex, which is considered to be a hydrogenation intermediate, is found by a neutron diffraction study [69,70]. For example,



Mn - C : 1.68 Å

Figure 14.6 Molecular structure of $(\eta^5\text{-}C_5H_5)(OC)_2Mn = C = CHPh$ [63].

$HMnRe(CO)_{14}$ forms an electron-deficient hydrogen-bridged bond with Mn and Re [69,70].



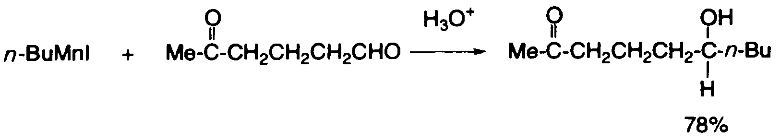
14.6 REACTION OF ORGANOMANGANESE COMPOUNDS

Representative reactions of organomanganese compounds are the following six reactions:

(1) Reaction with carbonyl compounds
(2) Cyclopentenelation (cyclopentaannulation)
(3) Reduction of vinyl halides
(4) Diene synthetic reactions
(5) Nucleophilic substitution reactions
(6) Others

14.6.1 REACTIONS WITH CARBONYL COMPOUNDS

Organomanganese compounds react with aldehydes, ketones and formic acid esters. In the esters, only formic acid esters are able to react. With an equivalent mixture of aldehyde and ketone, and a compound having these two kinds of functional groups, the organomanganese compounds react selectively with only the aldehyde group (formyl group) and the protection of the keto carbonyl group is not required. For example, with a keto aldehyde as shown in eq. (14.27), the organomanganese compounds react with the terminal CHO and give a secondary alcohol [71].

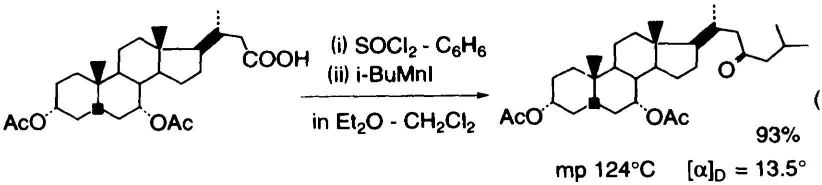


$$n\text{-BuMnI} + \text{Me-}\overset{O}{\overset{\|}{C}}\text{-CH}_2\text{CH}_2\text{CH}_2\text{CHO} \xrightarrow{H_3O^+} \text{Me-}\overset{O}{\overset{\|}{C}}\text{-CH}_2\text{CH}_2\text{CH}_2\text{-}\underset{H}{\overset{OH}{C}}\text{-}n\text{-Bu} \quad (14.27)$$

78%

Organomanganese compounds react with acid chlorides to afford ketones in high yields as shown in eq. (14.28). Thus reactions are able to proceed in many solvents. These reactions have a high selectivity to the functional groups, and are often available for a ketone synthesis [72–75]. For example, a steroid carboxylic acid reacts with $SOCl_2$ to afford an acid chloride, then organomanganese compounds react with the acid chloride to give a ketone by condensation reaction as shown in eq. (14.29). The alkyl derivatives of organomanganese compounds are liable as described above. Therefore, the alkyl derivatives are prepared by the reaction of manganese halide with organoalkali metal compounds or organomagnesium compounds and are used *in situ* without isolation [71,75].

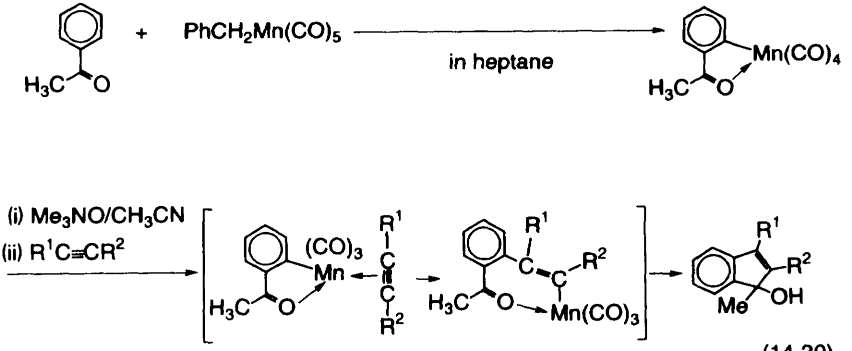
$$\mathrm{RMnI} + \mathrm{R'COCl} \xrightarrow[\text{in } Et_2O]{-10^\circ C\ -\ 20^\circ C} \underset{ca\ 90\%}{\mathrm{RCOR'}} \qquad (14.28)$$



(14.29)

14.6.2 CYCLOPENTANNELATION (CYCLOPENTAANNULATION)

Aryl-α-carbonyl compounds such as acetophenone, the cyclomanganation (orthomanganation) with manganesecarbonyl compounds easily proceeds as shown in eq. (14.17) as described above [76–81]. As shown in eq. (14.30), aryl-α-carbonyl compounds afford cyclomanganated compounds. Then triethylamine N-oxide reacts with the cyclomanganated compounds to afford the oxidative decarbonylation product. Finally, alkynes react with the decarbonylated products to give indene derivatives in high yields via alkyn π-complexes [76]. These reactions are highly regioselective. For example, the bulky alkyl or aryl of the alkyn preferentially bonds to a more remote position than the benzene ring, namely at the R^2 position.

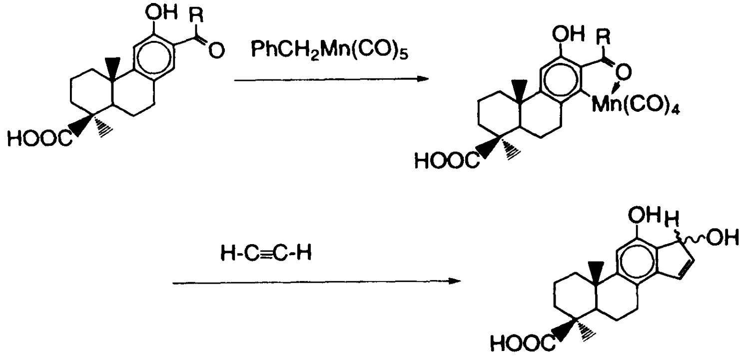


(14.30)

R^1, R^2 = H, Me, Et, Ph, $SiMe_3$, COOEt

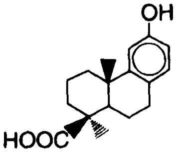
60 - 82%

For example, the cyclomangations of podocarpic acid α-carbonyl compound of diterpenoid easily proceed. Furthermore, the reaction of the above podocarpic acid derivative with an alkyn affords a steroid compound in a high yield by forming an indene ring as shown in eq. (14.31) [79,81].



(14.31)

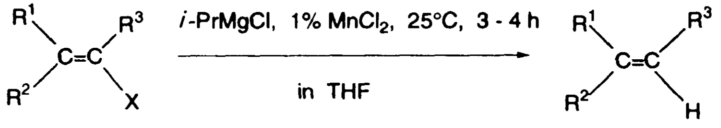
R = H 95%
R = Me 92%



podocarpic acid

14.6.3 REDUCTION OF VINYL HALIDES

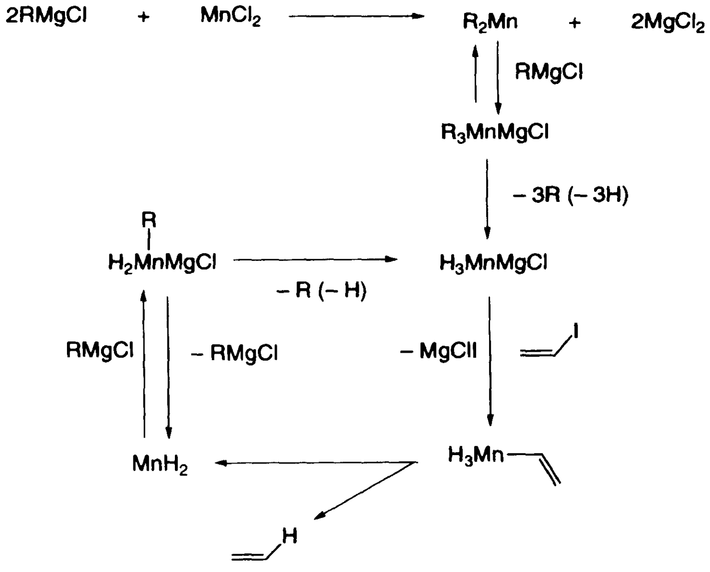
Vinyl halides are reduced with the complete retention of configuration of stereospecificity by reaction with Grignard reagents in the presence of a catalytic amounts of $MnCl_2$ in tetrahydrofuran solvent as shown in eq. (14.32) [72]. The reductions are thought that alkylmanganese compounds yielded by reaction with Grignard reagents are dealkylated by a β-elimination, and a selective hydrogenation with manganese hydride obtained proceeds as shown in Scheme 14.3 [82].



(14.32)

$R^1 - R^3$ = H, Et, Bu, Hexyl, Oct
X = Br, I

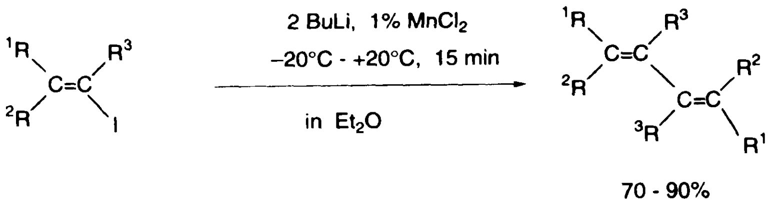
88 - 93%



Scheme 14.3 [82].

14.6.4 SYNTHETIC REACTION OF DIENES

Vinyl halides react with an alkyllithium in the presence of a catalytic amount of $MnCl_2$ to produce the diene by a coupling reaction with the complete retention of configuration as shown in eq. (14.33) [63,72,83]. In the reaction as shown in

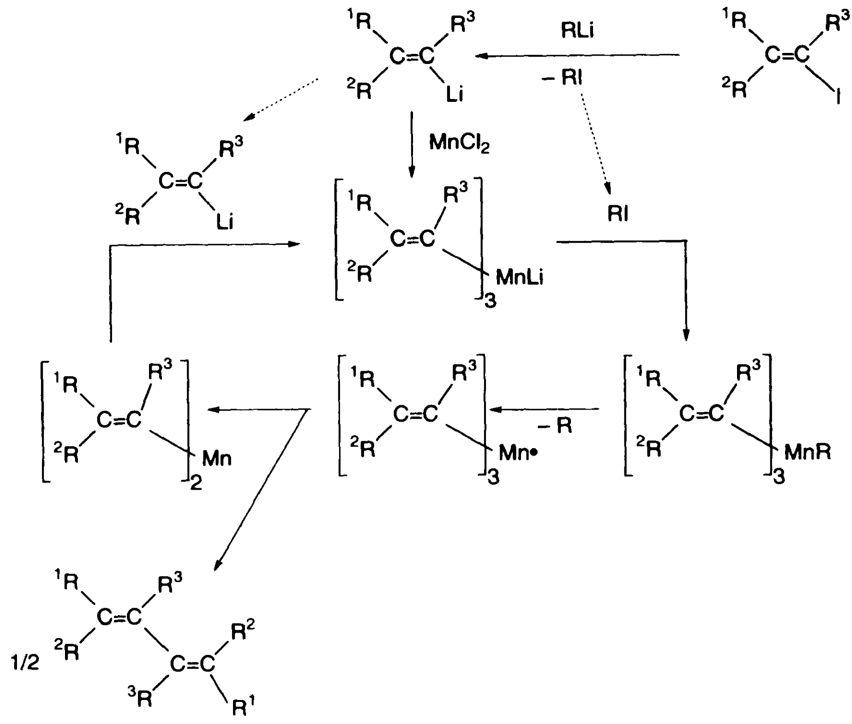


(14-33)

Scheme 14.4. Vinyl halides react with alkyllithium to afford vinyllithium, and then a reaction with $MnCl_2$ affords the manganeselithium compound. RI produced from the formation reaction of vinyllithium reacts with the manganeselithium compounds to afford the alkylmanganese compounds. The alkyl group of the alkylmanganese compounds is easily eliminated. Then the coupling reaction of one vinyl group eliminated produces $\frac{1}{2}$ mole of diene [83].

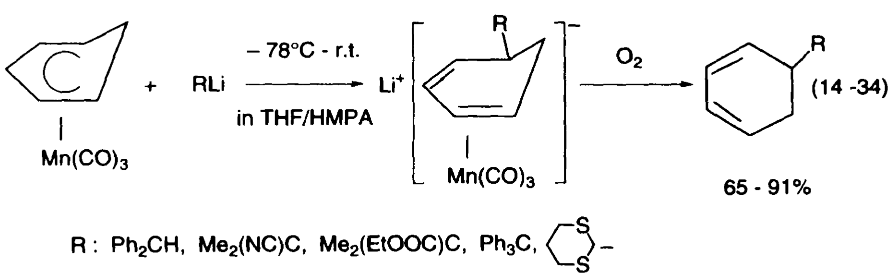
14.6.5 NUCLEOPHILIC SUBSTITUTION REACTIONS

η^5-Cyclohexadienyltricarbonyl manganese is an 18-electron compound and a stable compound as described above. For example, as shown in eq. (14.34), if it reacts with a nucleophile, a nucleophilic substitution reaction proceeds at the 5-position;



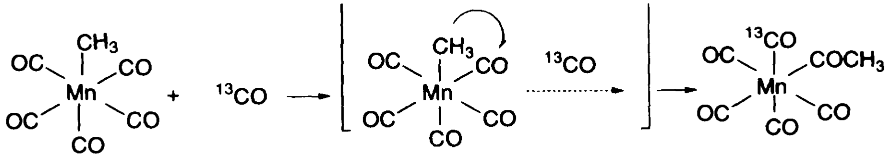
Scheme 14.4 [83].

then, with oxygen, the organomanganese compounds is decomposed to manganese carbonyl by oxidation, the nucleophilic substitution reaction product being given in 65–91% yield. The nucleophiles attack the cyclopendienyl ring from the opposite side to the $Mn(CO)_3$ group [84].



14.6.6 OTHERS

The carbonylation of organomanganesecarbonyl compounds have not known whether it is carbonyl insertion or alkylmigration. Then, ^{13}CO reacts with $MeMn(CO)_5$ and the product is investigated with IR spectroscopy. The product shows



Scheme 14.5 [85].

that methylmigration proceeds because the acetyl group does not contain a ^{13}CO group, the ^{13}CO contained in the carbonyl group at the *cis* position to the acetyl group [85].

REFERENCES

[1] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
[2] *Kagaku Daijiten*, Tokyo Kagaku Doojin, Tokyo, p. 2287, 1989.
[3] *Sekai Daihyakka Jiten*, Heibonsha, Tokyo, p. 243, 1988.
[3a] M. Kawahara, *Kagaku Kogyo*, **42** (1991) 22.
[4] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol. A16, p. 77, 1990.
[5] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd. ed., John Wiley, New York, vol. 14, p. 824, 1980.
[6] *12093 no Kagaku Shohin*, Kagaku Kogyo Nipposha, p. 153, 1993.
[7] *Kagaku Binran Ooyohen*, Japan Chemical Society, Maruzen, Tokyo, p. 315, 1980.
[8] *The Merck Index*, Merck, Rahway, 11th ed., p. 899, 1989.
[9] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, 4th ed., p. 1259, 1987.
[10] P.M. Treichel, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 4, p. 1, 1982.
[11] *Shin-jikken Kagaku Kouza 12, Yuki Kinzoku Kagaku*, Maruzen, Tokyo, p. 130, 1976.
[12] H.E. Podall, J.H. Dunn and H. Shapiro, *J. Am. Chem. Soc.*, **82** (1960) 1325.
[13] R.B. King, J.C. Stokes and T.F. Korenowski, *J. Organomet. Chem.*, **11** (1968) 641.
[14] H.E. Podall and A.P. Giraitis, *J. Org. Chem.*, **26** (1961) 2587.
[15] G. Wilkinson, F.A. Cotton and J.M. Birmingham, *J. Inorg. Nucl. Chem.*, **2** (1956) 95.
[16] J.L. Robbins, N.M. Edelstein, S.R. Cooper and J.C. Smart, *J. Am. Chem. Soc.*, **101** (1979) 3853.
[17] B.K. Bower and H.G. Tennent, *J. Am. Chem. Soc.*, **94** (1972) 2512.
[18] M. Tamura and J. Kochi, *J. Organomet. Chem.*, **29** (1971) 111.
[19] W.E. Billups, A.W. Moorehead, P.-J. Ko, J.L. Margrave, J.P. Bell and F.B. McCormick, *Organometallics*, **7** (1988) 2230.
[20] M.L.H. Green, D. O'Hare and J.M. Wallis, *J. Chem. Soc., Chem. Commun.*, (1984) 233.
[21] E.P. Kündig, P.L. Timms, B.A. Kelly and P. Woodward, *J. Chem. Soc. Dalton Trans.*, (1983) 901.
[22] E.O. Fisher and M.W. Schmidt, *Chem. Ber.*, **100** (1967) 3782.
[23] C. Elschenbroich and A. Saltzer, *Organometallics*, VCH, Weinheim, p. 234, 1989.
[23a] J.M. Andersen and J.R. Moss, *Adv. Organomet. Chem.*, **37** (1995) 169.
[24] G.A.M. Munro and P.L. Pauson, *Z. Anorg. Allg. Chem.*, **458** (1979) 211.

[25] D. Seyferth, E.W. Goldman and J. Pornet, *J. Organomet. Chem.*, **208** (1981) 189.

[26] D.H. Gibson, W.-L. Hsu and D.-S. Lin, *J. Organomet. Chem.*, **172** (1979) C7.

[27] K. Maruyama, T. Ito and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **52** (1979) 849.

[28] M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, **83** (1961) 825.

[29] I. Omae, *Organometallic Intramolecular-coordination Compounds, J. Organomet. Chem. Library 18*, Elsevier, Amsterdam, 1986.

[30] M.I. Bruce, *Angew. Chem.*, **89** (1977) 75.

[31] R.G. Little and R.J. Doedens, *Inorg. Chem.*, **12** (1973) 844.

[32] M.I. Bruce, B.L. Goodall, M.Z. Iqbal and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1971) 1595.

[33] R.G. Little and R.J. Doedens, *Inorg. Chem.*, **12** (1973) 840.

[34] R.J. McKinney, G. Firestein and H.D. Kaesz, *Inorg. Chem.*, **14** (1975) 2057.

[35] C.B. Knobler, S.S. Crawford and H.D. Kaesz, *Inorg. Chem.*, **14** (1975) 2062.

[36] N.P. Robinson, L. Main and B.K. Nicholson, *J. Organomet. Chem.*, **349** (1988) 209.

[37] R.L. Bennet, M.I. Bruce and I. Matsuda, *Aust. J. Chem.*, **28** (1975) 1256.

[38] R.J. Doedens, J.T. Veal and R.G. Little, *Inorg. Chem.*, **14** (1975) 1138.

[39] R.L. Bennett, M.I. Bruce and F.G.A. Stone, *J. Organomet. Chem.*, **94** (1975) 65.

[40] R.J. McKinney, R. Hoxmeier and H.D. Kaesz, *J. Am. Chem. Soc.*, **97** (1975) 3059.

[41] P. DeShong, D.R. Sidler and G.A. Slough, *Tetrahedron Lett.*, (1987) 2233.

[41a] R.D. Adams, L. Chen and W. Wu, *Organometallics*, **12** (1993) 4112.

[41b] M. Pfeffer, E.P. Urriolabeitia and J. Fischer, *Inorg. Chem.*, **34** (1995) 643.

[41c] R.D. Adams, G. Chen, L. Chen, W. Wu and J. Yin, *Organometallics*, **12** (1993) 3431.

[42] M.A. Bennet and R. Watt, *J. Chem. Soc., Chem. Commun.*, (1971) 94.

[43] R.J. McKinney and H.D. Kaesz, *J. Am. Chem. Soc.*, **97** (1975) 3066.

[44] B.L. Booth and E.J.R. Lewis, *J. Chem. Soc. Dalton Trans.*, (1982) 417.

[44a] M.I. Bruce, B.L. Goodall and F.G.A. Stone, *J. Organomet. Chem.*, **60** (1973) 343.

[45] W.J. Grigsby, L. Main and B.K. Nicholson, *Organometallics*, **12** (1993) 397.

[46] J.M. Villa, M. Gayoso, M.T. Pereira, M. López, G. Alonso, J.J. Fernández, *J. Organomet. Chem.*, **445** (1993) 287.

[47] M.Y. Darensbourg, D.J. Darensbourg and D. Drew, *J. Organomet. Chem.*, **73** (1974) C25.

[48] S. Onaka, N. Furuichi and Y. Tatematsu, *Bull. Chem. Soc. Jpn.*, **60** (1987) 2280.

[49] L.E. Manzer and L.J. Guggenberger, *J. Organomet. Chem.*, **139** (1977) C34.

[50] J.M. Cooney, L.M. Cooney, L.H.P. Gommans, L. Main and B.K. Nicholson, *J. Organomet. Chem.*, **349** (1988) 197.

[51] B.L. Booth and R.G. Hargreaves, *J. Chem. Soc. A*, (1970) 308.

[52] R.D. Adams, G. Chen, L. Chen, W. Wu and J. Yin, *J. Am. Chem. Soc.*, **113** (1991) 9406.

[53] A. Shakoor, K. Jacob and K.-H. Thiele, *Z. Anorg. Allg. Chem.*, **489** (1983) 115.

[54] H. Alper, *J. Organomet. Chem.*, **73** (1974) 359.

[55] M.R. Churchill, K.N. Amoh and H.J. Wasserman, *Inorg. Chem.*, **20** (1981) 1609.

[56] A. Márquez, J.F. Sanz, M. Gelizé, *J. Organomet. Chem.*, **434** (1992) 235.

[57] K. March, J. Nováková and J.B. Raynor, *J. Organomet. Chem.*, **439** (1992) 341.

[58] J.L. Latten, R.S. Dickson, G.B. Deacon, B.O. West and E.R.T. Tiekink, *J. Organomet. Chem.*, **435** (1992) 101.

[59] R.A. Andersen, E. Carmona-Guzman, J.F. Gibson and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, (1976) 2204.

[60] D. O'Hare, V. Murphy, A. Bland and P. Scott, *J. Organomet. Chem.*, **443** (1993) C37.

[61] D.P. Freyberg, J.L. Robbins, K.N. Raymond and J.C. Smart, *J. Am. Chem. Soc.*, **104**, (1979) 892.

[61a] E.O. Fischer and S. Breitshaft, *Chem. Ber.*, **99** (1966) 2213.

[61b] M. Herberhold, T. Hofmann, W. Milius and B. Wrackmeyer, *J. Organomet. Chem.*, **472** (1994) 175.

[61c] B. Wrackmeyer, T. Hofmann and M. Herberhold, *J. Organomet. Chem.*, **486** (1995) 255.

[62] A.B. Antonova, N.E. Kolobova, P.V. Petrovsky, B.V. Lokshin and N.S. Obezyuk, *J. Organomet. Chem.*, **137** (1977) 55.

[63] A.N. Nesmeyanov, G.G. Aleksandrov, A.B. Antonova, K.N. Anisimov, N.E. Kolobova and Yu. T. Struchkov, *J. Organomet. Chem.*, **110** (1976) C36.

[64] W. Strohmeier and H. Hellmann, *Chem. Ber.*, **98** (1965) 1598.

[65] J.Y. Le Marouille, C. Lelay, A. Benoit, D. Grandjean, D. Touchard, H. Le Bozec and P. Dixneuf, *J. Organomet. Chem.*, **191** (1980) 133.

[66] P. Friedrich, G. Besl, E.O. Fischer and G. Huttner, *J. Organomet. Chem.*, **139** (1977) C68.

[67] C. Kelley, N. Lugan, M.R. Terry, G.L. Geoffroy, B.S. Haggerty and A.L. Rheingold, *J. Am. Chem. Soc.*, **114** (1992) 6735.

[68] U. Kirchgässner, H. Piana and U. Schubert, *J. Am. Chem. Soc.*, **113** (1991) 2228.

[68a] D.J. Cardin, B. Cetinkaya and M.F. Lappert, *Chem. Rev.*, **72** (1972) 545.

[68b] D.J. Cardin, B. Cetinkaya, M.J. Doyle and M.F. Lappert, *Chem. Soc. Rev.*, **2** (1973) 99.

[68c] M.R. Terry, C. Kelley, N. Lugan, G.L. Geoffroy, B.S. Haggerty and A.L. Rheingold, *Organometallics*, **12** (1993) 3607.

[68d] M.R. Terry, L.A. Mercando, C. Kelley, G.L. Geoffroy, P. Nombel, N. Lugan, R. Mathieu, R.L. Ostrander, B.E. Owens-Waltermire and A.L. Rheingold, *Organometallics*, **13** (1994) 843.

[68e] M. Akita, N. Ishi, A. Takabuch, M. Tanaka and Y. Moro-oka, *Organometallics*, **13** (1994) 258.

[69] A. Albinati, R.M. Bullock, B. Rappoli and T.F. Koetzle, *Inorg. Chem.*, **30** (1991) 1414.

[70] R.M. Bullock, L. Brammer, A.J. Schultz, A. Albinati and T.F. Koetzle, *J. Am. Chem. Soc.*, **114** (1992) 5125.

[71] G. Cahiez and J.F. Normant, *Tetrahedron Lett.*, (1977) 3383.

[72] J.F. Normant (translator: K. Utimoto), *Kagaku Zokan*, **99** (1983) 135.

[73] G. Cahiez, A. Masuda, D. Bernard and J.F. Normant, *Tetrahedron Lett.*, (1976) 3155.

[74] G. Cahiez, *Tetrahedron Lett.*, (1981) 1239.

[75] G. Cahiez, D. Bernard and J.K. Normant, *Synthesis*, (1977) 130.

[76] L.S. Liebeskind, J.R. Gasdaska, J.S. McCallum and S.J. Tremont, *J. Org. Chem.*, **54** (1989) 669.

[77] N.P. Robinson, L. Main and B.K. Nicholson, *J. Organomet. Chem.*, **364** (1989) C37.

[78] R.C. Cambie, M.R. Metzler, P.S. Rutledge and P.D. Woodgate, *J. Organomet. Chem.*, **381** (1990) C26.

[79] R.C. Cambie, M.R. Metzler, P.S. Rutledge and P.D. Woodgate, *J. Organomet. Chem.*, **389** (1990) C22.

[80] R.C. Cambie, M.R. Metzler, P.S. Rutledge and P.D. Woodgate, *J. Organomet. Chem.*, **429** (1992) 41.

[81] R.C. Cambie, M.R. Metzler, C.E.F. Rickard, P.S. Rutledge and P.D. Woodgate, *J. Organomet. Chem.*, **431** (1992) 177.

[82] G. Cahiez, D. Bernard and J.F. Normant, *J. Organomet. Chem.*, **113** (1976) 107.

[83] G. Cahiez, D. Bernard and J.F. Normant, *J. Organomet. Chem.*, **113** (1976) 99.

[84] B.C. Roell, Jr., K.F. McDaniel, W.S. Vaughan and T.S. Macy, *Organometallics*, **12** (1993) 224.

[85] K. Noack and F. Calderazzo, *J. Organomet. Chem.*, **10** (1967) 101.

15 Organoiron Compounds

15.1 INTRODUCTION

The use of iron is thought to have begun later than bronze, since heating at ca. 1500 °C (the melting point of iron) is technically difficult in ancient times. But, recently, the reduction of iron was found to be begun at the temperature of the melting point of copper (1083 °C), and the use of iron is confirmed from some unearthed items that the use of iron began earlier than thought. As the oldest example, the oldest ironware which is thought to be artificial was excavated at Semarra in Mesopotamia and was made about 5000 BC.

From ca. 5000 BC to ca. 3000 BC, unearthed items of both artificial and meteoric iron were found. Meteoric iron comes from meteorites and contains 4–16% of Ni and a small amount of cobalt, carbon and sulfur. As the major component is iron, meteoric iron was used as an iron alloy [1].

Iron exists in a comparatively large amount relative to copper and tin, and as the steel is hard and has high strength, it is excellent as weapon material. The use of iron is a key for the expansion of the country from ancient times. Iron is also the most used metallic element nowadays.

As organoiron compounds, $Fe(CO)_5$ was largely used as an antiknock agent since 1925. However, its use continued until tetraethyllead was widely used. In 1951, stable ferrocene was found and these two compounds are used as the basic compound of organoiron compounds because of easy handling and its low price. Therefore, organoiron compounds have very much been studied as organometallic compounds.

15.2 IRON

Iron belongs to group 8 of the periodic table, and the outer electron configuration is $3d^6 4s^2$. It exists as 4.1%, the fourth most abundant element in the Earth's crust, outranked only by aluminum, silicon and oxygen [2].

The atomic nucleus $^{56}_{20}Fe$ is the most stable element with respect to energy. It is thought that iron is after magnesium as the most abundant metal element in the universe, and is a major component of the inner core of the Earth [3].

Hematite (Fe_2O_3), magnetite (Fe_3O_4) and pyrite (FeS) are the main ores of iron. Pig iron is produced by reduction of these ores with coke, and steel is produced by removing carbon and silicon by oxidation with air or oxygen in a revolving furnace, open-hearth furnace or electric furnace.

The properties of iron are shown in Table 15.1 [3–6]. Iron shows ferromagnetism at ordinary temperatures and it is called α-iron. At temperatures higher than the Curie temperature (760 °C), it transforms to β-iron showing paramagnetism, and at higher than 910 °C, it transforms to γ-iron, and at higher than 1400 °C it transforms to δ-iron.

Iron is a white, lustrous metal and has a high ductility and malleability. Iron is liable to react with oxygen. Iron powder is ignited in oxygen. At high temperatures, with oxygen, iron yields Fe_2O_3 and with high temperature steam it yields Fe_3O_4.

Iron reacts violently with chlorine, sulfur and phosphorus. It is readily dissolved in a dilute mineral acid, but, with an oxidizing acid such as concentrated nitric acid, it forms a protective layer of iron oxide, and becomes passive [3].

Iron as steel is used in the equipment parts of machines, civil engineering, construction industry, transportation, etc. As in alloy, nickel steel in armor plate, manganese alloy in rails, silicon steel having electromagnetic properties, tungsten steel for a high speed cutting tool, and stainless steel, etc., have been widely used.

Iron oxide, iron sulfide, iron chloride, yellow prussiate of sodium ($Na_4Fe(CN)_6 \cdot 10H_2O$) and iron nitrate as inorganic iron compounds are used in pigments, paints, magnetic materials, treatment of waste water and catalysts, etc.

Table 15.1 Properties of Iron [3–6]

Property	Value
melting point, °C	1539
boiling point, °C	2880
crystal structure	body centered cubic
transformation temperature (°C)	
α-Fe→β-Fe (Curie point)	760
β-Fe→γ-Fe (face centered cubic)	910
γ-Fe→δ-Fe (body centrered cubic)	1400
latent heat of fusion, $J\,g^{-1}$	15.28
latent heat of vaporization, $J\,g^{-1}$	340.4
density, 20 °C, g/cm^3	7.87
specific heat at 100 °C, $J\,g^{-1}$	0.50
hardness	
Mohs scale	4.5
Brinell hardness	44–55 HB
coefficient of thermal expansion, at 0–800 °C, $10^{-6}K^{-1}$	14.5
electrical resistivity at 20 °C, $10^{-8}\Omega m$	9.71
thermal conductivity, at 0 °C, $W\,m^{-1}K^{-1}$	79

$Fe(CO)_5$, as an organoiron compound described above, was used as antiknock agent. Nowadays it is used for the production of pure fine iron particles by its decomposition at 300 °C or higher. This pure iron is used for the iron core of an electromagnet, alloying agents, additives for mineral enriched foods, pharmaceutical additives, reducing agents, fillers for rubber sheets or plastic sheets as microwave attenuating material [4].

Iron oxide is produced by the combustion of $Fe(CO)_5$ with excess air. The iron oxide produced is used for a highly transparent red pigment and a highly pure ferrite, Fe_3O_4 or γ-Fe_2O_3 is freely produced with a different treatment temperatures. If $Fe(CO)_5$ is decomposed in a magnetic field, high intensity crystalline iron whiskers are produced and these whiskers are used for composite materials or catalysts [4].

15.3 PREPARATION OF ORGANOIRON COMPOUNDS

Organoiron compounds are prepared by the following five reaction methods.

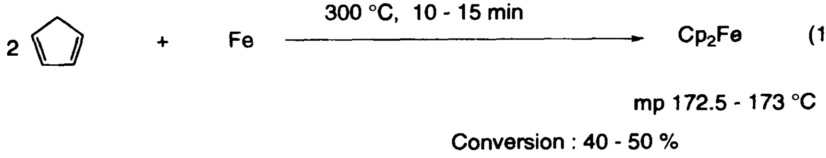
(1) Direct reaction process
(2) Reactions with organoalkali metal compounds or with Grignard reagents
(3) Reactions with ironcarbonyl compounds
(4) Reactions with ferrocene type compounds
(5) Others

15.3.1 DIRECT REACTION PROCESS

$Fe(CO)_5$ is prepared by the direct reaction of activated iron with carbon monoxide as shown in eq. (15.1). Activated iron is obtained by the reduction of $Fe_2(CO)_9$ or Fe_2O_3 with hydrogen or by concussion of iron powder in a heptane solution under hydrogen sulfide atmosphere [7].

$$\mathrm{Fe} \quad + \quad \mathrm{CO} \quad \xrightarrow[\text{atmospheric pressure}]{\text{room temp., 20 h}} \quad \mathrm{Fe(CO)_5} \qquad (15.1)$$

Ferrocene is prepared in 40–50% conversion by the reaction of activated iron obtained by the reaction of iron oxide with hydrogen, with cyclopentadiene as shown in eq. (15.2) by Miller, Tebboth and Tremaine [8] in 1952. Ferrocene synthesis by this direct reaction process, was published later than the reaction with



(15.2)

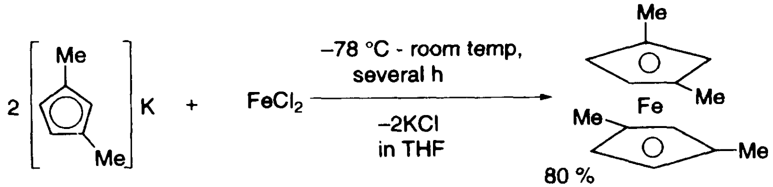
Grignard reagents as shown in eq. (15.5) by Keal and Pauson [9] described below. However, the submission of the manuscript was earlier by one month. Both of these two studies were done early in 1950's.

15.3.2 REACTIONS WITH ORGANOALKALI METAL COMPOUNDS OR WITH GRIGNARD REAGENTS

Various kinds of organoiron compounds are prepared by the reaction of ferrous chloride with organoalkali metal compounds such as organolithium compounds, organosodium compounds and organopotassium compounds or with Grignard reagents. For example, high purity bisindenyliron is prepared by reacting indenylsodium with ferrous chloride in a tetrahydrofuran solvent. Removing the solvent under reduced pressure, extracting with pentane, cooling at −78 °C, crystallizing out and subliming was done as shown in eq. (15.3) [10]. The indene has two rings of benzene and cyclopentadienyl rings and the bisindenyliron is the compound having a sandwich structure with cyclopentadienyl rings.

$$\mathrm{FeCl_2} + \underset{\text{sodium indenide}}{\mathrm{2C_9H_7Na}} \xrightarrow[\substack{\text{in THF}\\ \text{yield 26.5 \%}}]{\text{reflux , 16 h}} \underset{\substack{\text{mp 184 -185 °C}\\ \text{sublimation : 130 °C/0.25 mm Hg}}}{(\mathrm{C_9H_7})_2\mathrm{Fe}} + \mathrm{2NaCl} \qquad (15.3)$$

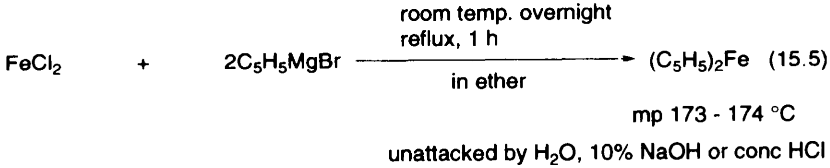
In the case of using an organopotassium compound, 2,4-dimethylcyclopentadienylpotassium is cooled and added to a ferrous chloride tetrahydrofuran solution and reacted at room temperatures for several hours to afford organoiron compounds as shown in eq. (15.4). The crystal is purified by recrystallization with hexane or by sublimation [11].



(15.4)

If the mixture of cyclopentadienyllithium and the phenylazo derivative (Li-C_5H_5-N = N-Ph) reacts with ferrous chloride, ferrocene and the ferrocene phenyldiazo derivative (η^5-C_5H_5)Fe(η^5-C_5H_5-N = N-Ph, 18%) is produced [11,12].

As described above, Kealy and Pauson [9] published in *Nature* in 1951 that ferrocene is prepared by the reaction of ferrous chloride with Grignard reagents. The purpose of the reaction was to synthesize liable fulvalene. However, the product was very stable. From the analytical data, it is thought that it is the σ-bond compound of two cyclopentadiene rings and iron or the complex of two aromatic cyclopentadienyl anions and Fe^{2+}.



$$\underset{}{FeCl_2} + 2C_5H_5MgBr \xrightarrow[\text{in ether}]{\text{room temp. overnight, reflux, 1 h}} \underset{\substack{\text{mp 173 - 174 °C} \\ \text{unattacked by } H_2O\text{, 10\% NaOH or conc HCl}}}{(C_5H_5)_2Fe} \quad (15.5)$$

15.3.3 REACTIONS WITH IRONCARBONYL COMPOUNDS

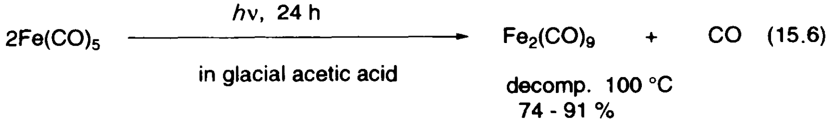
$Fe(CO)_5$, the most basic compound of the organoiron compounds, is widely available for the syntheses of other organoiron compounds. $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, besides $Fe(CO)_5$, are also used for the synthesis of organoiron compounds.

$Fe(CO)_5$ is a stable compound. It does not react with air at room temperatures and under light irradiation $Fe_2(CO)_9$ gradually increases. $Fe(CO)_5$ is decomposed at 100 °C or higher in the absence of high pressure carbon monoxide to form a filmy iron [13].

$Fe_2(CO)_9$ is very useful as a source of the $Fe(CO)_3$ and $Fe(CO)_4$ moieties in synthesis. Its solubility in various kinds of solvents is low. Its reactivity is higher than that of $Fe(CO)_5$, and is also higher than that of $Fe_3(CO)_{12}$ in many reactions. For example, with alkenes, $Fe_2(CO)_9$ reacts at room temperatures, $Fe_3(CO)_{12}$ reacts at 60–100 °C and $Fe(CO)_5$ reacts at about 150 °C under UV irradiation. $Fe_2(CO)_9$ shows high reactivity even if in the absence of a solvent [13].

$Fe_3(CO)_{12}$ displays some solubility in a wider variety of organic solvents compared with $Fe_2(CO)_9$. Its reactivity is higher than that of $Fe(CO)_5$. It is slowly oxidized by air. It is slightly thermally unstable at room temperature. One of the reaction products of this thermal decomposition appears to be finely divided iron [13].

$Fe_2(CO)_9$ (diiron enneacarbonyl) is prepared by the reaction of $Fe(CO)_5$ under UV irradiation as shown in eq. (15.6) [14]. $Fe_3(CO)_{12}$ is also prepared from $Fe(CO)_5$ as shown in eq. (15.7). $Fe(CO)_5$ reacts with triethylamine at 80 °C and then cooled at room temperatures to afford a dark brown amine complex $(Et_3NH)(Fe_3H(CO)_{11})$. $Fe_3(CO)_{12}$ is obtained as a dark green solid by the reaction of the amine complex with HCl. As $Fe_3(CO)_{12}$ (triiron dodecacarbonyl) is slightly thermally unstable at room temperatures as described above it should therefore be stored in a cold dark place under an inert atmosphere [15,16].

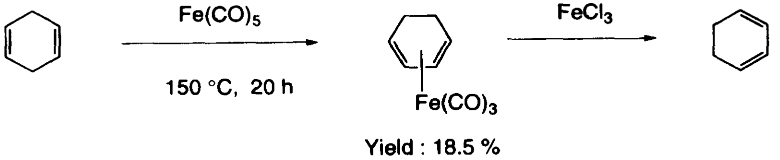


$$2Fe(CO)_5 \xrightarrow[\text{in glacial acetic acid}]{h\nu\text{, 24 h}} \underset{\substack{\text{decomp. 100 °C} \\ \text{74 - 91 \%}}}{Fe_2(CO)_9} + CO \quad (15.6)$$

$$3Fe(CO)_5 + N(C_2H_5)_3 + 2H_2O \xrightarrow{80\ ^\circ C} [(C_2H_5)_3NH][Fe_3H(CO)_{11}] + 2CO_2 + 2CO + H_2$$

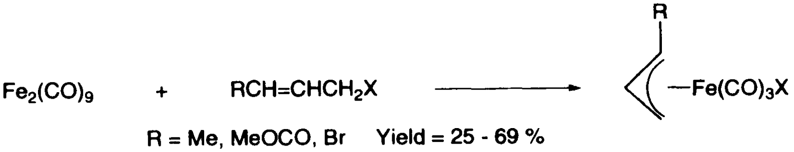
$$12[(C_2H_5)_3NH][Fe_3H(CO)_{11}] + 18HCl \xrightarrow{100\ ^\circ C,\ \text{several h}} \underset{76\%}{11Fe_3(CO)_{12}} + 15H_2 + 3FeCl_2 + 12(C_2H_5)_3NHCl \qquad (15.7)$$

With Fe(CO)$_5$, the coupling reaction and the isomerization of alkenes or alkynes proceed. Carbonyl insertion tends to proceed during these reactions [17]. In the reaction of alkenes, the reaction with conjugate dienes is especially liable to proceed. Therefore, non-conjugated dienes such as 1.4-cyclohexadiene isomerize to the conjugate dienes such as 1,3-cyclohexadiene to which Fe(CO)$_5$ is easily coordinated as shown in eq. (15.8) [13,15,17–21].

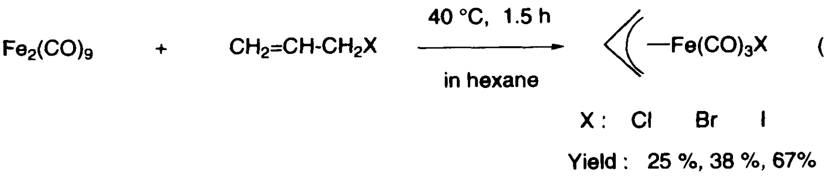


(15.8)

With Fe$_2$(CO)$_9$, an oxidative elimination is liable to proceed. Reaction examples of the oxidative elimination are shown in eqs. (15.9) and (15.10) [13,15,22].



(15.9)



(15.10)

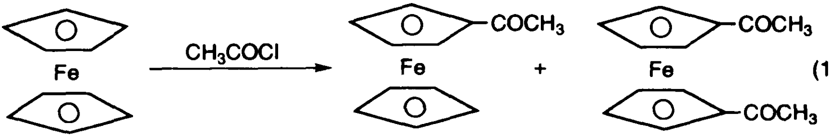
Decarbonylation proceeds with an alkali metal complex of Fe$_3$(CO)$_{12}$ as shown in eq. (15.11) [23,24].

$$Fe_3(CO)_{12} \xrightarrow{\text{(1) Na/Hg} \quad \text{(2) RCOCl, h}\nu} cis\text{-}[R_2Fe(CO)_4] \qquad (15.11)$$

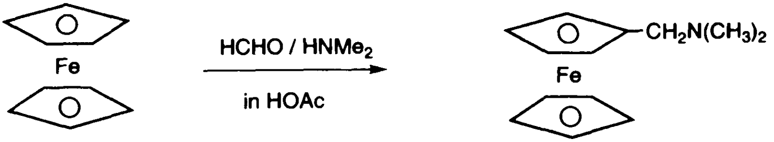
15.3.4 REACTIONS WITH FERROCENE TYPE COMPOUNDS

Ferrocene is easily prepared by the direct reaction process or by a reaction with Grignard reagents as shown in eqs. (15.2) and (15.5). Keal and Pauson [9] and Miller [8] found that ferrocene is stable in water, 10% NaOH aqueous solution, and concentrated hydrochloride acid at around the boiling point. It sublimates at 100 °C without decomposition and is stable up to 470 °C under a nitrogen atmosphere. It dissolves in organic solvents such as alcohol, ether and benzene. As a solid and a solution it is stable in air [8,9,25].

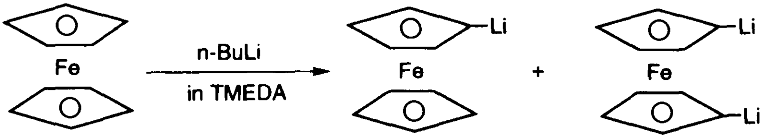
Ferrocene is an aromatic compound similar to benzene. As the aromatic rings of ferrocene are coordinated by iron, ferrocene shows a higher basicity than that of benzene. Then an electrophilic reaction is liable to proceed. For example, Friedel–Crafts acylation, Mannich reaction (aminomethylation) and lithiation easily proceeds as shown in eqs. (15.12)–(15.14) [26].



(15-12)



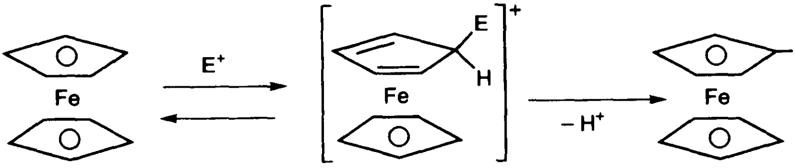
(15-13)



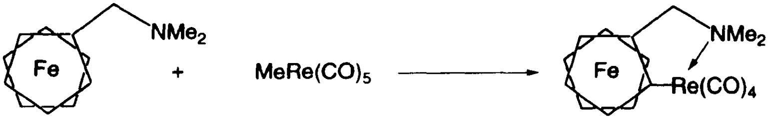
(15-14)

TMEDA : Tetramethyleneethylenediamine
$Me_2CH_2CH_2Me_2$

The cyclopentadiene ring of ferrocene has a partially anionic charge, different from benzene ring. So η^5-C_5H_5-Fe-η^5-$C_5H_4NH_2$ is more basic than aniline and the acidity of η^5-C_5H_5-Fe-η^5-C_5H_4COOH is lower than that of benzoic acid. Hence ferrocene acts as an electron donor. Therefore, the electrophilic substitution reaction on ferrocene is liable to proceed faster compared with benzene (the rate of reaction in ferrocene is 3×10^6 time than that of benzene [26]). The electrophilic substitution reaction of ferrocene is shown by reactions with electrophiles such CH_3COCl (eq. (15.12)), HCHO (eq. (15.13)) and *n*-BuLi (eq. (15.14)), and by the following metalation reactions as shown in eqs. (15.15) and (15.16).

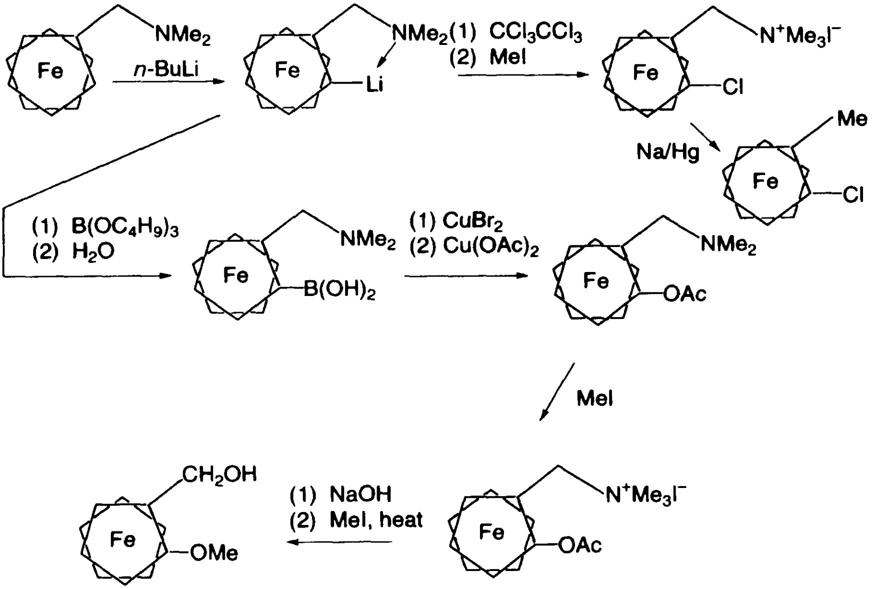


(15-15)



(15.16)

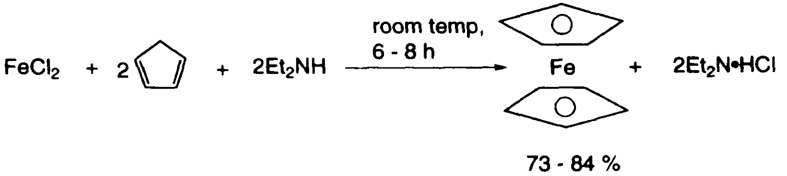
The dimethylaminomethylferrocene obtained by aminomethylation is shown in eq. (15.13), the metalation at the 2-position corresponding to the orthometalation of benzene is liable to proceed [26–30], for example, as shown in eq. (15.16) and Scheme 15.1. The metalation at the 2-position is able to proceed selectively and the metal is able to be exchanged easily with other substituents. Further, as the dimethylaminomethyl group is easily able to be exchanged with a variety of functional groups such as methyl, methylol and formyl. So the dimethylaminomethylferrocene is used as the raw material for the synthesis of ferrocene derivatives [27,29].



Scheme 15.1 [29].

15.3.5 OTHERS

Four synthetic processes of organoiron compounds have been described. The second reaction with organoalkali metal compounds or Grignard reagents are processes where the organometallic compounds are used as a dehalogenation agent. Amines, $AlCl_3$, $NaBH_4$ and KOH are also used as the dehalogenation agent. For example, ferrocene is easily prepared with an amine as the dehalogenation agent as shown in eq. (15.17) [15,31]. The reactions with $AlCl_3$ (eq. (15.18)) [15,32–34] and $NaBH_4$ (eq. (15.19)) [15,35] and KOH (eq. (15.20) [36] as the dehalogenation agent are shown, respectively. The reaction with $NaBH_4$ affords a nitrogen complex as shown in eq. (15.19).



(15.17)

$$C_6H_6 + FeCl_3 \xrightarrow{\text{reflux}} C_6H_5Cl + FeCl_2 + HCl$$

excess

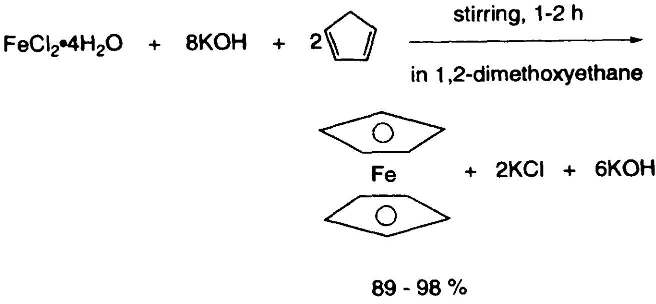
$$2C_6H_6 + FeCl_2 + 2AlCl_3 \longrightarrow [Fe(C_6H_6)_2][AlCl_4]_2$$

$$[Fe(C_6H_6)_2][AlCl_4]_2 \xrightarrow{H_2O,\ NH_4PF_6} [Fe(C_6H_6)_2][PF_6]_2 \qquad (15.18)$$

yield 79 %

$$FeCl_2{\bullet}2H_2O + 3PC_2H_5Ph_2 \xrightarrow[\text{in } Et_2O]{NaBH_4,\ -10\ ^\circ C,\ 5\ h} \xrightarrow[\text{in petrolem ether}]{N_2,\ \text{room temp.}} FeH_2(N_2)(PC_2H_5Ph_2)_3 \qquad (15.19)$$

69.5 %



(15.20)

15.4 STRUCTURES OF ORGANOIRON COMPOUNDS

Ferrocene has high stability and its paramagnetic and dipole moment are almost zero. From IR and UV spectra, Wilkinson and co-workers [37] speculated a staggered structure (Figure 15.1) in which two cyclopentadienyl rings are parallel and have point symmetry. After that, it was proved by X-ray diffraction studies [38–41]. The difference of energy of the staggered and eclipsed forms is calculated to be small, only 4 kJ/mole or less [26].

Gaseous ferrocene at 140 °C is eclipsed (D_{5h}). However, $(\eta^5\text{-}C_5H_5)_2Fe$ is staggered (D_{5d}) in both the solid and gaseous state. The hydrogens of ferrocene are in the same plane as the cyclopentadienyl ring [42–46]. The distance between the two cyclopentadienyl rings of ferrocene is 3.32 Å [43]. Various kinds of ferrocene derivatives in which the two rings are bonded with an element such as carbon or a metal have been synthesized. These bridged ferrocenes are called ferrocenophanes. If the two cyclopentadienyl rings are bonded with three carbons (3C chain), the bond length is shorter than the distance between the two rings of ferrocene. Then the two rings tilt slightly. However, with four carbons (4C chain), the two rings have no strain and are parallel. Ferrocene bonded with five carbon chains is called superferrocenophane. Hisatome and co-workers [47–49] have synthesized the superferrocenophane of five 4C chains and the structure is determined by X-ray diffraction studies. The superferrocenophane of 4C chain is shown in Figure 15.2 and is eclipsed at $n = 4$ [49].

For the bridge formation of synthesized ferrocenophanes the following three methods are used.

(1) A chain is bonded to one ring, and the terminal of the chain is bonded to the other ring by an intramolecular substitution reaction.
(2) Each ring is bonded to each chain and two chains, each bonded to a ring, are bonded by condensation at the end of chains.
(3) Ferrocenophanes are directly prepared by metalation of dicyclopentadienyl derivatives [49,50].

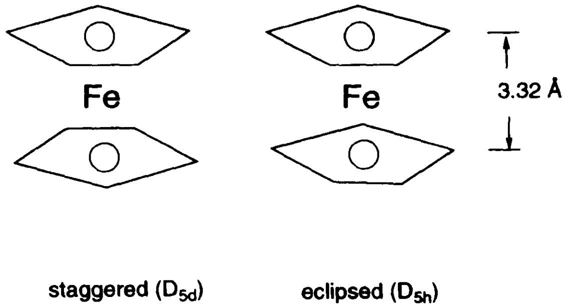


Figure 15.1 Configuration of $(\eta^5\text{-}C_5H_5)_2Fe$ [37].

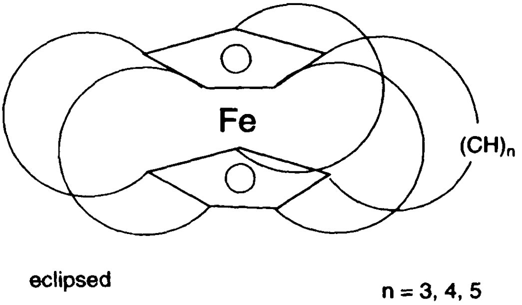


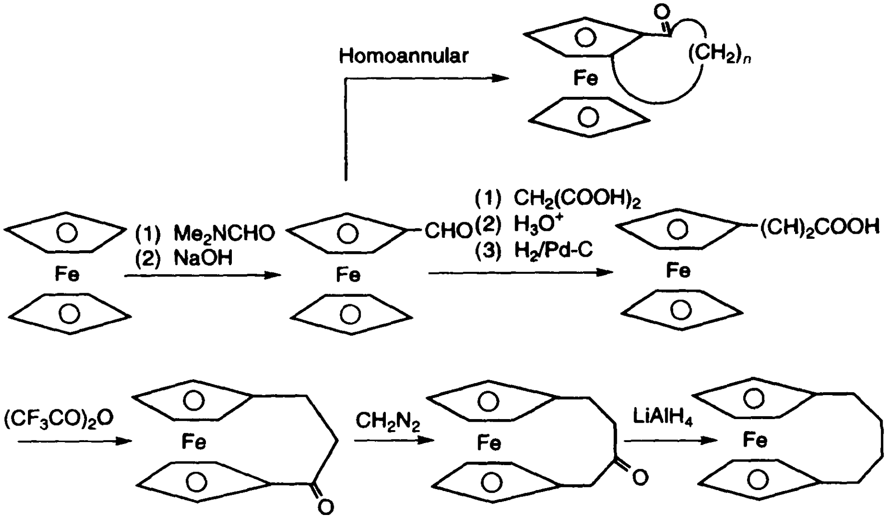
Figure 15.2 Structure of superferrocenophane [47–49].

As the second and third processes are difficult to selectively form many bridges for the synthesis of superferrocenophane, superferrocenophane is synthesized by the first process.

In the synthesis of many bridged compounds, as shown in Scheme 15.2 in the case of a 4C chain, at first the 3C chain is synthesized and the 4C chain is obtained by ring expansion reaction of the 3C chain by treatment of diazomethane.

If the 4C chain is synthesized first, the bridge structure is not formed due to a homoannular reaction as shown in Scheme 15.2 [51].

When the number of the bridge increases, a conventional process gradually does not tend to proceed. For example, trifluoroacetic acid anhydride, which is used in the first bridge formation reaction, is changed to polyphosphoric acid or poly-



Scheme 15.2 [47,51].

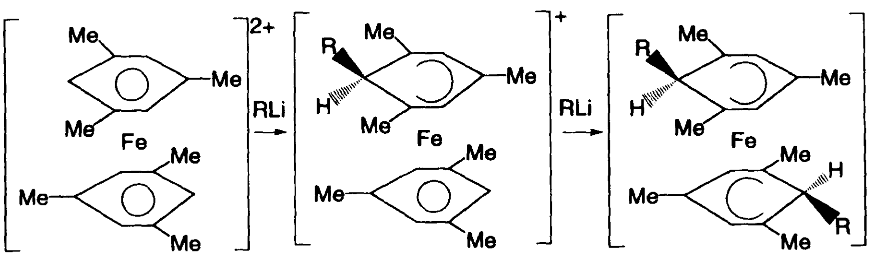
phosphoric acid ester and diazomethane has to be used after formation of a BF_3 complex of the substrate, in place of the direct diazomethane reaction in the ring expansion reaction [47].

Hisatome and co-workers also synthesized superferrocenophane of four 3C chains and one 4C chain, and ferrocenophane of four 5C chains [47–47b].

The length of the two cyclopentadienyl rings of 4C superferrocenophane is 3.244 Å, and it is shorter than that of ferrocene (3.32 Å). α-Carbon of a methylene chain is displaced to exo by 0.13–0.16 Å from the Cp ring. The thermal vibrations of the β-methylene carbons on the bridge are large and remarkably anisotropic and by MM2′ calculation the zigzag structure is stable by 148 kcal/mol than the eclipsed linear methylene chain as shown in Figure 15.2 [47]. In the bridge of two cyclopentadienyl rings, the rings tilt when they bond with three carbon chains, and with two one-carbon chains, the tilt of the rings increases by decreasing the number of the chain carbon. The elements of the bridge are metal elements such as Si [52–56a], Ge [54–56b], Sn [56], As [56], Mn [57], Ti [56], Zr [56], Hf [58], W [59], Ni [56], Pd [56], Pt [60–60b], Au [60c] and Ag [60d], and non-metallic elements such as S [60e–60f] and P [54,56,57] besides carbon. These structures have been determined by X-ray diffraction studies.

In the bonding of ironcarbonyls with carbon–carbon unsaturated compounds as shown in Table 15.2 [56,61–65], one double bond and four carbonyls and two double bonds and three carbonyls form 18-electron compounds. However, one π-allyl and four carbonyls and, one cyclopentadienyl and three carbonyls form 19-electron compounds. Then iron becomes Fe^+ by liberating one electron.

1,3,5-Trimethylbenzene has three electron-donating methyl groups and it is liable to form η^6-complexes compared with benzene. However, in the case of iron complexes, it is liable to form Fe^{2+} complexes as shown in Table 15.2 and eq. (15.21), and the reaction with organolithium compound yields a ferrocene-like sandwich structure by the alkylation of the benzene ring [66].



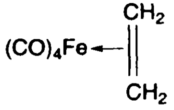
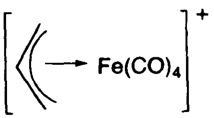
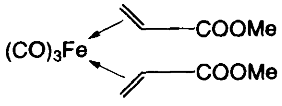
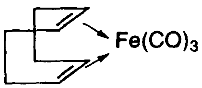
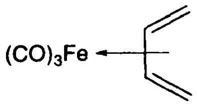
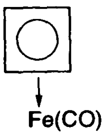
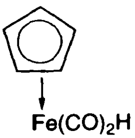
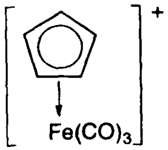
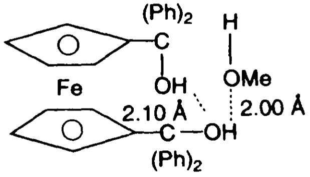
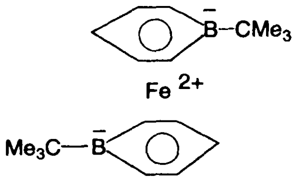
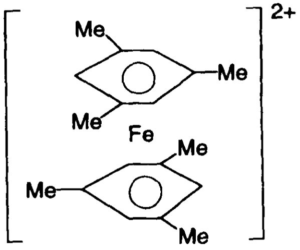
Yield
R = Ph (38 %), t-Bu (80 %)

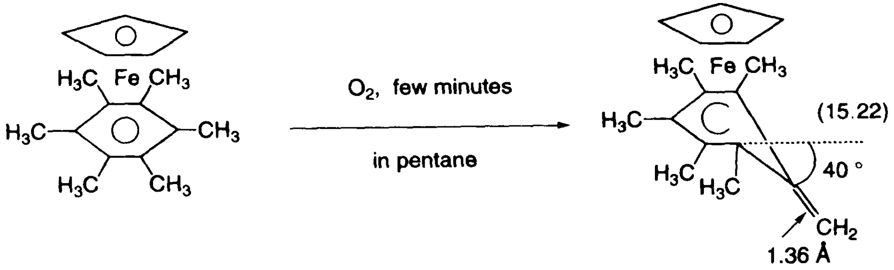
Yield
R = Ph (57 %), t-Bu (75 %)

(15.21)

As hexamethylbenzene has six electron-donating methyl groups, it is liable to form a η^6-complex compared with 1,3,5-trimethylbenzene, and it forms 19-electron compounds as shown in eq. (15.22). However, it is labile, even at −78 °C, and it transforms to the 18-electron bispentadienyl complexes (eq. (15.22)) [67].

Table 15.2 Some examples of η^n-organoiron compounds [56,61–65]

η^2		η^3	
η^4			
			
η^5			
η^6			



(15.22)

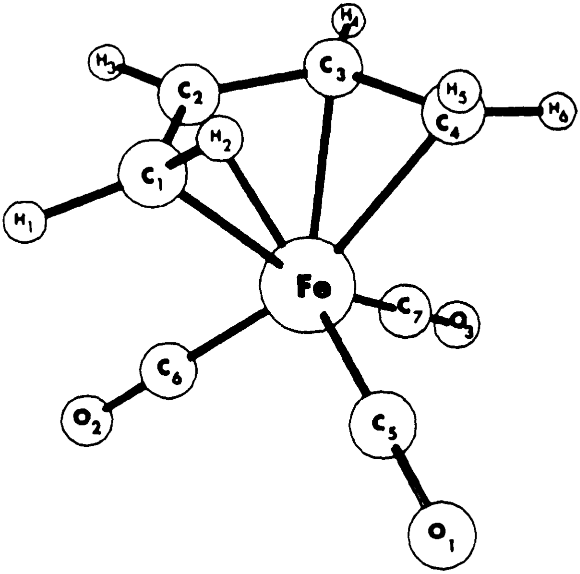
Borabenzene ($C_5H_5BR^-$) (see Table 15.2) is an anion which tends to form a η^6-complex and iron bonds to two borabenzene anions to form a η^6-complex of Fe^{2+} [63].

A butadieneiron complex forms a *cis* structure. The hydrogen of the terminal carbon forms the bond to the metal element. However, hydrogen from another terminal carbon does not form an intramolecular hydrogen bond since the terminal carbon is rotated by 28° out of the butadiene plane [62].

The methanol adduct of the ferrocene bisdiphenylmethylalcohol derivative forms an intramolecular hydrogen bond and an intermolecular hydrogen bond with methanol oxygen as shown in Table 15.2. The bond length of the intermolecular hydrogen bond is shorter by 0.1 Å. This evidence is thought to be caused due to the degree of freedom of the intermolecular hydrogen bond being higher than that of intramolecular hydrogen bond [64].

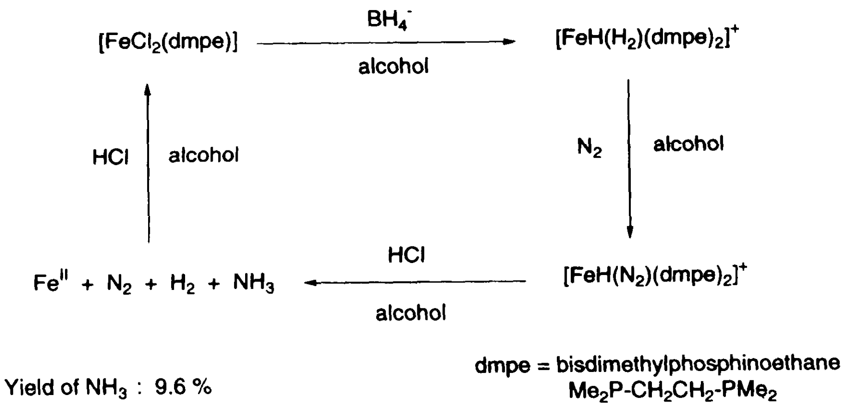
The active center of Mo–Fe nitrogenase of a nitrogen fixation enzyme is thought to be a metal–hydrogen bond. The investigation of MoH_3 did not give any evidence, but reaction with FeH_3 produced NH_3 of nitrogen fixation product as shown in Scheme 15.3 [68].

The structures of these iron hydride and nitrogen compounds are shown in Figure 15.4 and Figure 15.5, respectively [68]. The hydride shown in Figure 15.4



Fe - H : 2.65 Å

Figure 15.3 Structure of (butadiene)iron tricarbanoyl determined from microwave measurements [62].



Scheme 15.3 [68].

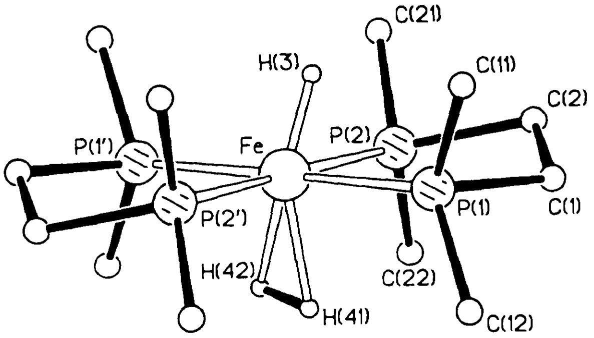


Figure 15.4 Structure of $[FeH(H_2)(dmpe)_2]^+ BF_4^-$ [68].

has a side-on type structure and the nitride shown in Figure 15.5 has an end-on linear structure [68]

15.5 PREPARATION OF ORGANOIRON COMPOUNDS

The basic compounds of syntheses of organoiron compounds are two compounds of ferrocene and ironpentacarbonyl compounds. As many reactions have also been studied of these two compounds, first the author will describe reactions with these compounds and then describe cyclometalations polymerizations, catalytic reactions, etc.

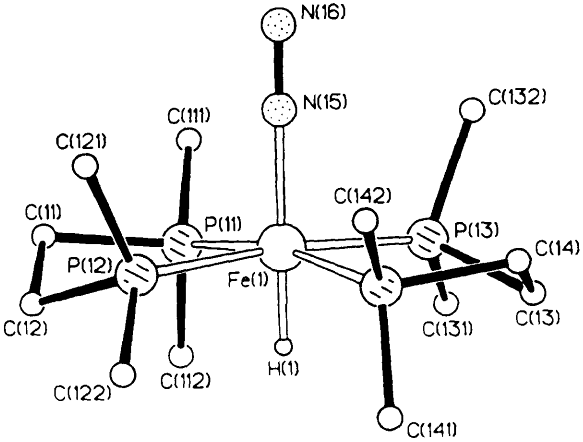
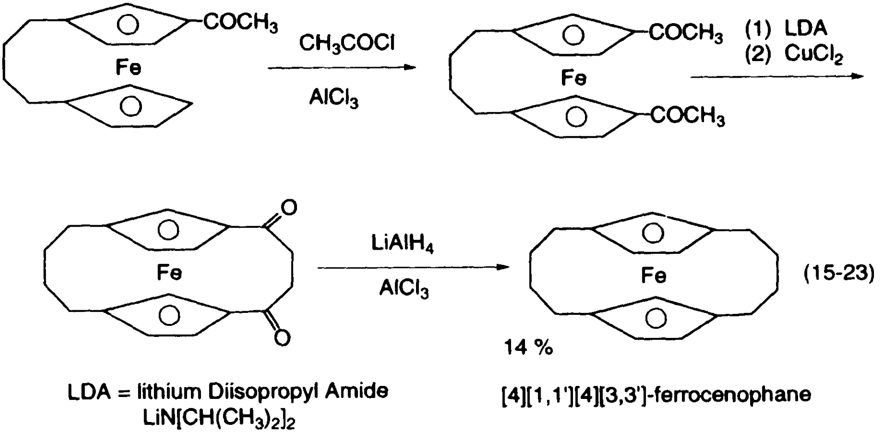


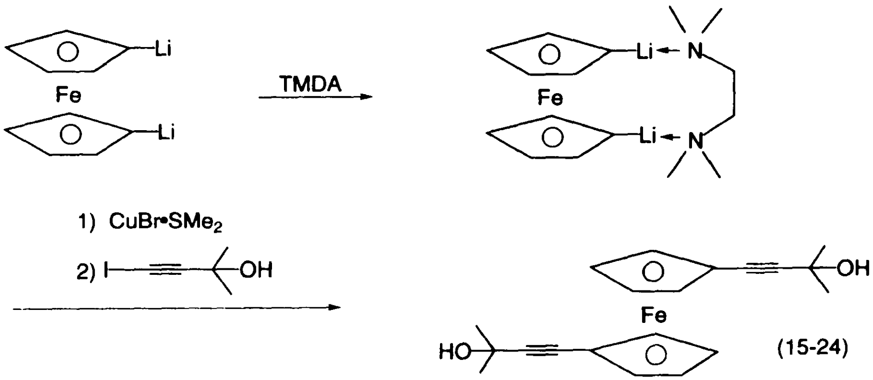
Figure 15.5 Structure of $[FeH(N_2)(dmpe)_2]^+ BF_4^-$ [68].

15.5.1 REACTIONS OF FERROCENE TYPE COMPOUNDS

Ferrocenes are aromatic compounds similar to benzene, as they have a high basicity, electrophilic substitution reactions such as Friedel–Crafts acylation (eq. (15.12)), metalation (eqs. (15.14) and (15.16), Scheme 15.1), Mannich reaction (aminomethylation, eq. (15.13)) and formylation (Scheme 15.1) are liable to proceed as described above. These products also have a high reactivity and they are used as raw materials for other ferrocene derivatives as shown in Schemes 15.1 and 15.2. For example, if one bridged ferrocene is obtained from Scheme 15.1 to form another bridge, lithium diisopropylamide (LDA) is reacted, oxidized with $CuCl_2$, and reduced with $LiAlH_4$ to afford a two bridged ferrocenophane as shown in eq. (15.23) [50,69].

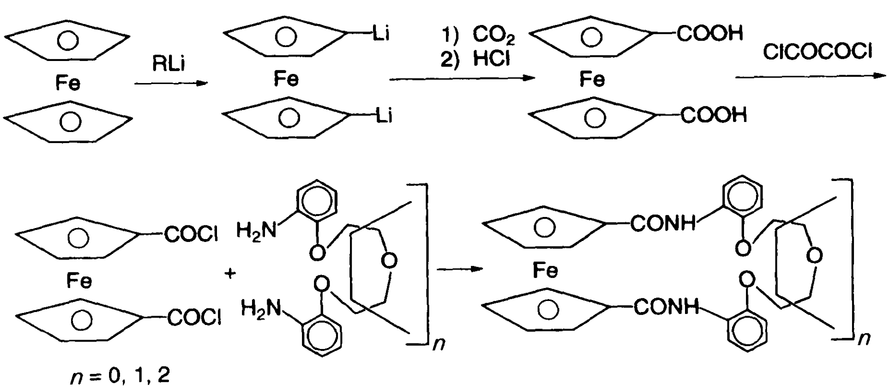


If ferrocene reacts with organolithium compounds, lithium bonds to one cyclopentadienyl ring. However, in the reaction with excess organolithium compounds, another lithium bonds to another cyclopentadienyl ring as shown in eq. (15.24). The dilithium compound is protected with tetramethylenediaminoethane, reacted with CuBr, and then with an iodide to afford various kinds of ferrocene derivatives by condensation as shown in eq. (15.24) [70,71].

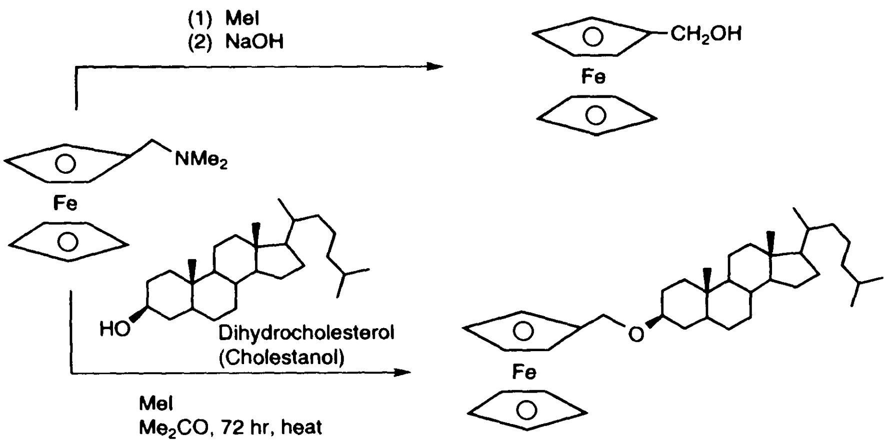


(15-24)

The dilithium compound reacts with carbon dioxide, and an acid is added to afford a dicarboxylic acid. The dicarboxylic acid reacts with ClCOCOCl to afford two acid chlorides. The two acid chlorides are easily condensed with diamino compounds to afford the bridged compound. The reaction with monoamine yields simply diamide. The amide is reduced with $LiAlH_4$ to afford a diamino derivative. If a monolithium compound is used as the starting material, these products are the monoamide and monoamine, respectively. By using these reaction, various kinds of ferrocene derivatives such as crownethers and sulfur-containing compounds have been synthesized [72–76].



Scheme 15.4 [56,72].



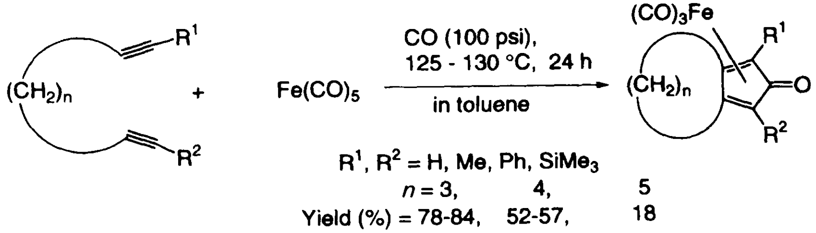
Scheme 15.5 [76,77].

Aminomethylated compounds (eqs. (15.13) and (15.16), Scheme 15.1) obtained by the Mannich reaction yield various kinds of 2-metalated compounds. The aminomethylated compounds yield quaternary amine salts by the Menshutkin reaction with an alkyl halide, and a methylol derivative is prepared by adding alkali to the salt. Dihydrocholesterol (cholestanol) reacts with dimethylaminomethylferrocene in the presence of methyl iodide and acetone to afford the ferrocene derivatives as shown in Scheme 15.5 [76,77].

15.5.2 REACTION OF IRONCARBONYL COMPOUNDS

Ironcarbonyl compounds are liable to form π-complexes with unsaturated compounds such as monoenes, butadiene, cyclobutadienes, and cyclopentadiene. In the case of diene, the two double bonds of 1,5-cyclooctadiene are able to coordinate to the metal, without a sterical strain as shown in Table 15.2. The two double bonds of 1,4-cyclohexadiene are difficult to bond to iron without strain, so 1,4-cyclohexadiene isomerized to 1,3-cyclohexadiene. The iron atoms have such a high reactivity with diene compounds that the isomerization of the diene occurs [13,19,20,25].

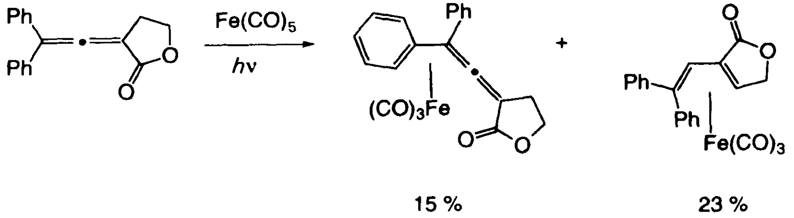
The reactivity of iron with a carbon–carbon unsaturated bond is also shown in an intramolecular carbonylative coupling [78,78a] as shown in eq. (15.25), and on reactions with vinylketenes, vinylallene and vinylketenimine, etc. as shown in Scheme 15.6 and eqs. (15.26) and (15.27). In the formation of a methylene chain cyclic compound shown in eq. (15.25), the five-membered ring is more liable to form than six- or seven-membered ring [78].



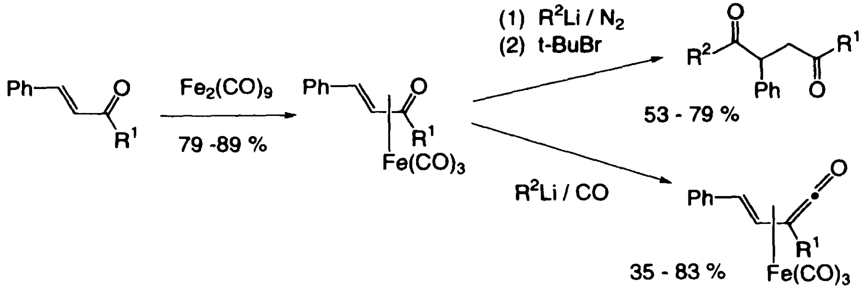
(15.25)

Vinylketone easily reacts with $Fe_2(CO)_9$ to afford an oxadiene π-complex in high yield as shown in Scheme 15.6. The π-complex reacts with an alkyllithium under nitrogen atmosphere to afford 1,4-diketone. However, under a carbon monoxide atmosphere vinylketene is obtained as shown in Scheme 15.6 [79,80]. The formation of the 1,4-diketone, as shown in Scheme 15.7 [80], is at first the alkylanion to the carbonyl carbon with the addition of alkyllithium to form iron carbene, and the metathesis of the iron carbene with $C=C$ proceeds. On the other hand, under a carbon monoxide atmosphere, the metathesis of the iron carbene with $C=O$ proceeds, the alkyl group of alkyllithium is eliminated as a carboxylic acid to form an iron carbene, and reacts with carbon monoxide to afford a vinyl ketene as shown in Scheme 15.7 [80].

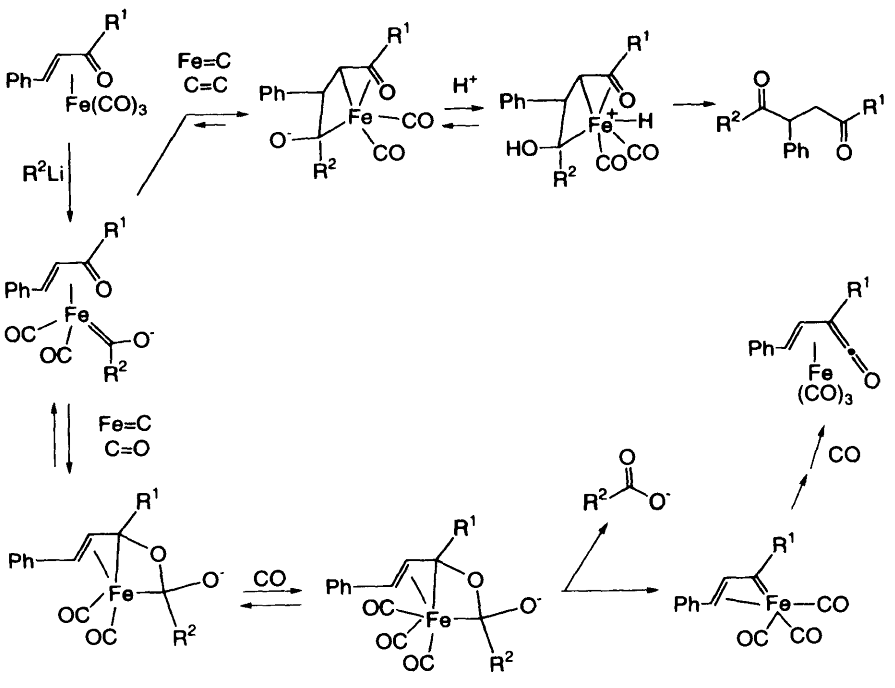
As shown in eq. (15.26), the iron atom of iron carbonyl is able to form the η^4-complex with benzene double bonds and allene double bonds, or carbonyl double



(15.26)



Scheme 15.6 [79,80].

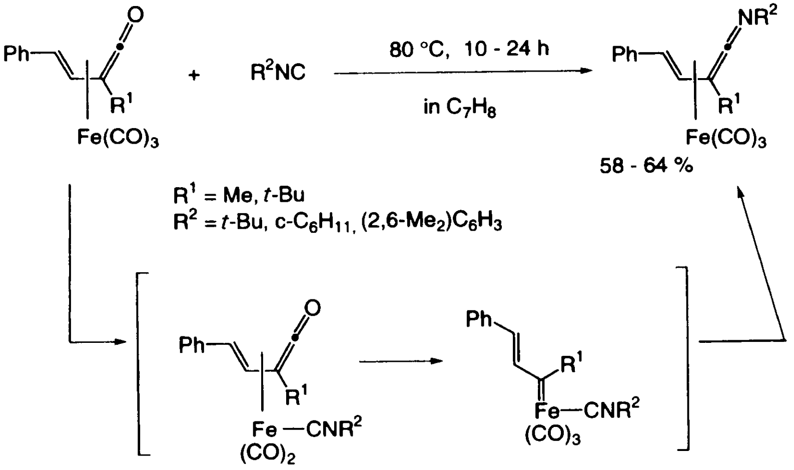


Scheme 15.7 [80].

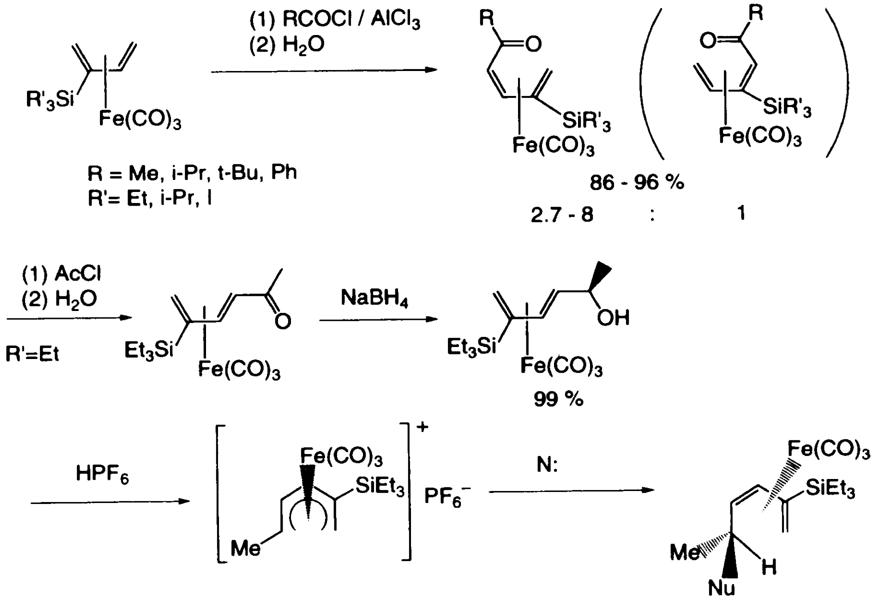
bonds and allene double bonds. Actually, the reaction under light irradiation forms the η^4-complex of the former benzene double bond and allene double bond, and another η^4-complex is also yielded with two double bonds by the rearrangement of the allene [80,81].

As shown in eq. (15.27), vinylketene reacts with isonitrile to afford the iron-carbonyl complex of vinylketeimine. If the reaction is stopped at the initial stage (3–3.5 h), the intermediate product in which one carbonyl group is replaced with isonitrile forms with the same amount of the final product. The intermediate is rearranged to a keteimine via an iron carbene complex as shown in eq. (15.27) [80].

As shown in Scheme 15.8, if 1,3-butadiene iron complex is acylated, the diene is protected and the one terminal carbon is acylated. Further reaction with $NaBH_4$ means the acyl group is selectively and quantitatively reduced to the hydroxy group while protecting the carbon–carbon double bond. The treatment with HPF_6 yields a pale yellow cation. The nucleophilic substitution reaction of the 5-carbon of the cation is liable to proceed: the nucleophile attacks the back side of the iron to produce the exo product as shown in Scheme 15.8 [82,83].



(15.27)



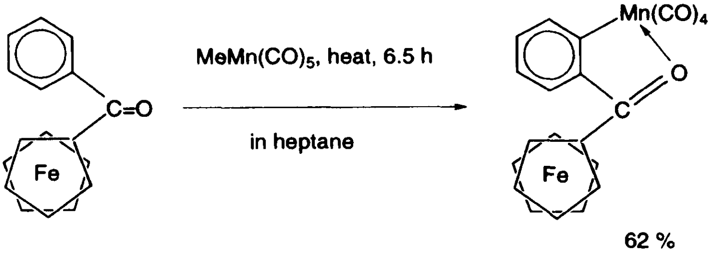
Nucleophiles =	NaBH$_3$CN,	PPh$_3$,	Me$_2$CuLi,	NaCH(COOMe)$_2$
N: =	H,	PPh$_3$,	Me,	CH(COOMe)$_2$
Yield (%) =	62	71	46	71

Scheme 15.8 [82,83].

15.5.3 CYCLOMETALATION

Aminomethyl compounds obtained by the Mannich reaction (eq. (15.13)) are the representative compounds of cyclometalation. They easily produce five-membered ring compounds containing metal atoms such as Re and Li as shown in eq. (15.16) and Scheme 15.1. These five-membered ring compounds are prepared not only from aminomethyl compounds but also carbonyl, thiocarbonyl and oxymethyl compounds as shown in Table 15.3 [27,56,84].

As the cyclometalations selectively metalated at the 2-position, it is used for the synthetic reaction of ferrocene derivatives as shown in Scheme 15.1. The representative cyclometalation is called an orthometalation, it is the metalation of a benzene ring at the ortho-position. Metalation at the 2-position of ferrocene corresponds to the orthometalation of the benzene ring. A reaction shown in eq. (15.28) shows the difference of reactivity of a benzene ring and ferrocene ring.



(15.28)

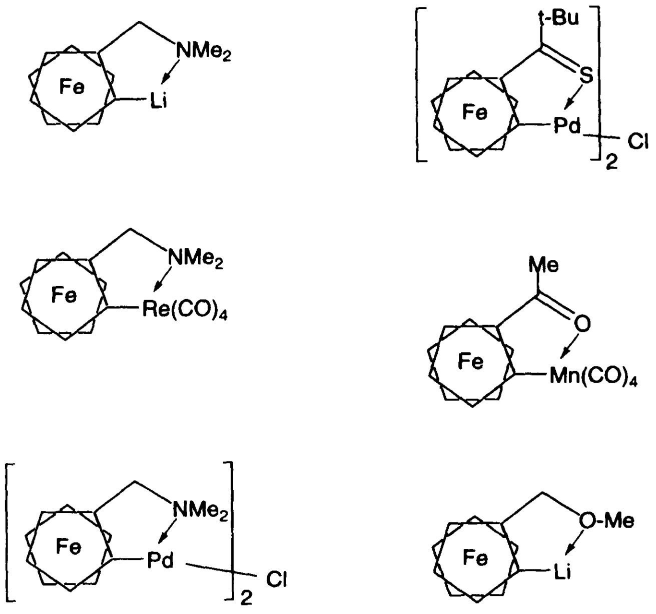
Actually, cyclometalation of a benzene ring proceeds [30]. The ferrocene ring has a high basicity because of the coordination of iron atom. hence, in the case of simple metalation, ferrocene reacts more easily than benzene [85]. But it is thought that the strain of the five-membered ring attached to benzene is less than that of ferrocene since cyclometalation of benzene actually proceeds [86].

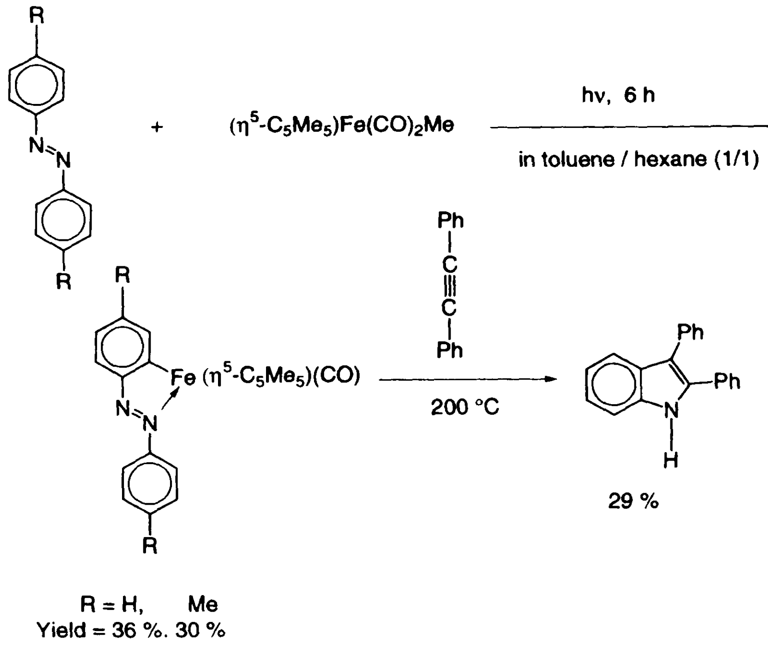
Diazobenzene is also a compound in which cyclometalation easily proceeds, as shown in eq. (15.29) and cyclometalated compounds are prepared by heating or light irradiation [87]. The five-membered ring compounds reacts with diphenylacetylene with heating or light irradiation to afford 2,3-diphenylindol as shown in eq. (15.29) [88].

15.5.4 POLYMERIZATION

As ferrocene has a similar reactivity to benzene, the various kinds of polymerizations also proceed similarly to compounds having a benzene ring. The representative reactions are shown in eqs. (15.30)–(15.35). The reaction shown in eq. (15.30) is the polymerization of a vinyl monomer similar to styrene. On the ferrocene vinyl monomer, the addition polymerization proceeds as shown in eq.

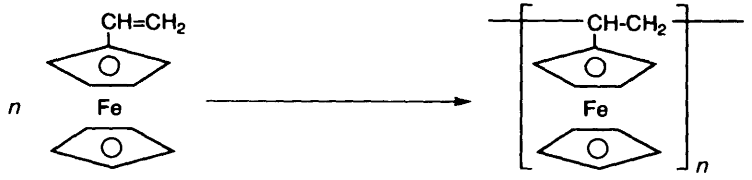
Table 15.3 Five-membered ring compounds prepared by cyclometalation [27,56,84]



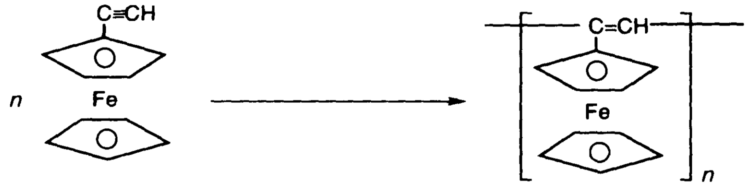


(15.29)

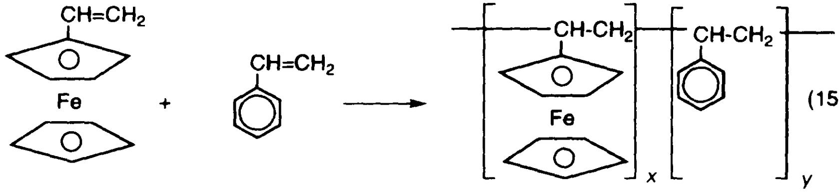
(15.30), and copolymerizations with other vinyl monomers proceeds as shown in eq. (15.32) and copolymerizations with the other organometallic vinyl monomers also proceed as shown in eq. (15.33) [89].



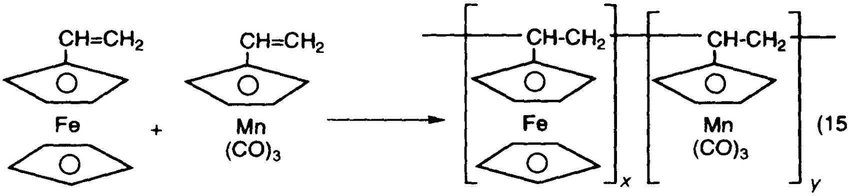
(15.30)



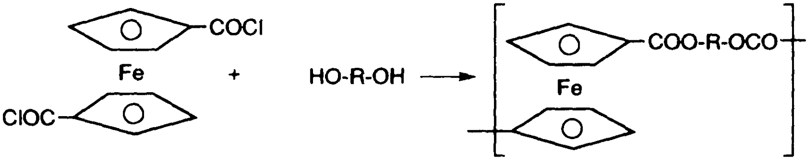
(15.31)



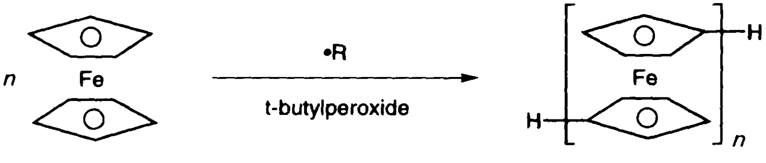
(15.32)



(15.33)

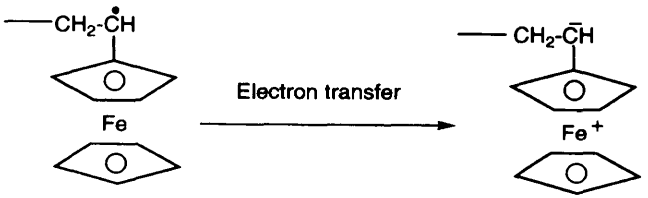


(15.34)

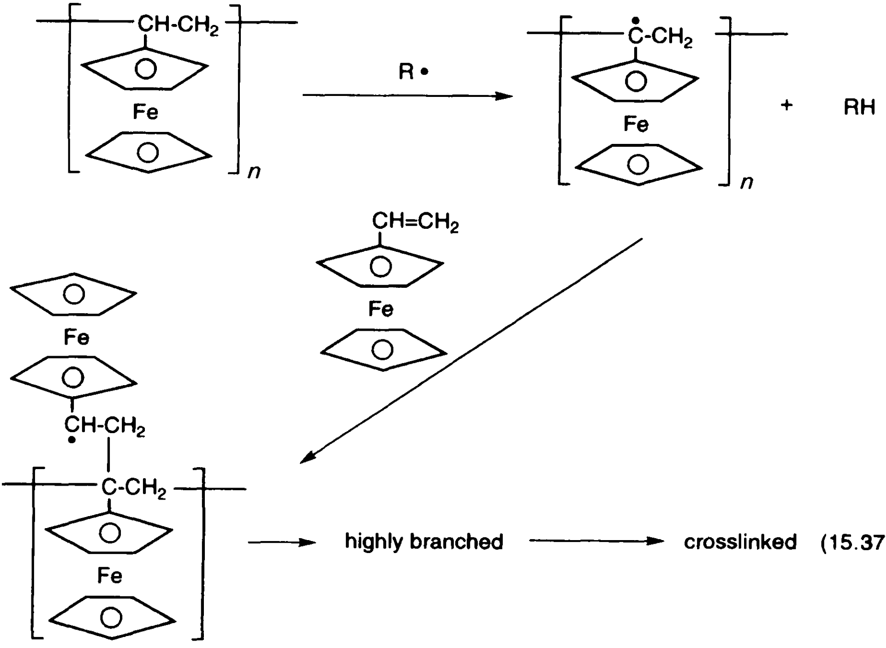


(15.35)

Vinylferrocene (eq. (15.30)) is polymerized by using radical, cation, anion or Ziegler type catalysts as initiators. The polymerization with azobisisobutyronitrile as the radical initiator yields a polymer having an average molecular weight of ca. 50000, but the polymerization with a cation or Ziegler type initiator yields only a polymer having the molecular weight of ca. 2000–4000. In the polymerization of vinylferrocene, the degree of polymerization is proportional to the monomer concentration at the start. The termination of polymerization is an intramolecular electron transfer as shown in eq. (15.36) [89–91]. A branch is thought to be formed by eliminating the hydrogen of the ferrocenylethyl group at the α-position as shown in eq. (15.37) [91].



(15.36)



(15.37)

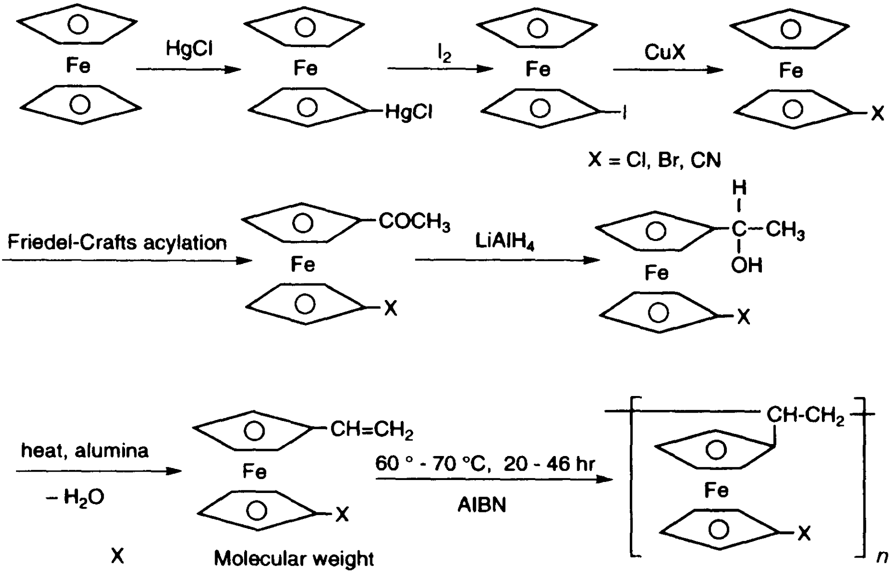
Polyvinylferrocene is a yellow to brown solid, the softening temperatures of a high molecular polymer is ca. 300 °C, it is thermally stable, and it is stable to air in solution. It is gradually decomposed in a halide solvent. It decomposes rapidly under light irradiation, dissolves in solvents such as carbon disulfide, benzene and chloroform, and does not dissolve in ethyl acetate, hexane and methanol, etc. [89].

As shown in eq. (15.31), ethynylferrocene polymerizes similar to vinylferrocene with various kinds of initiators, and most of the polymers are insoluble. As the polymer has an all conjugated structure, electroconductivity is expected. But actually the electroconductivity is almost the same as an insulator; however, it is partially oxidized with iodine or dichlorodicyanoquinone and when Fe(III) is 40–60%, the electroconductivity is 10^{-6}–$10^{-7}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ [89,92].

The other vinyl monomers as shown in eq. (15.30) are acryl, metacryl, or vinylcarbonylferrocene derivatives. The condensation polymers shown in eq. (15.34), e.g., polyesters, polyamides, polyketones, polyazomethine and polyazine, have been reported [89]. Examples of synthesis of vinyl monomers and their polymerization are shown in Scheme 15.9 [93].

Phosphazene reacts with alkyllithium to afford a pendant methylanion and the anion reacts with ferrocenylketone to afford the pendant polymer. The substitution ratio of pendant groups is 36–45% and its molecular weight is 150000–200000 [94,95].

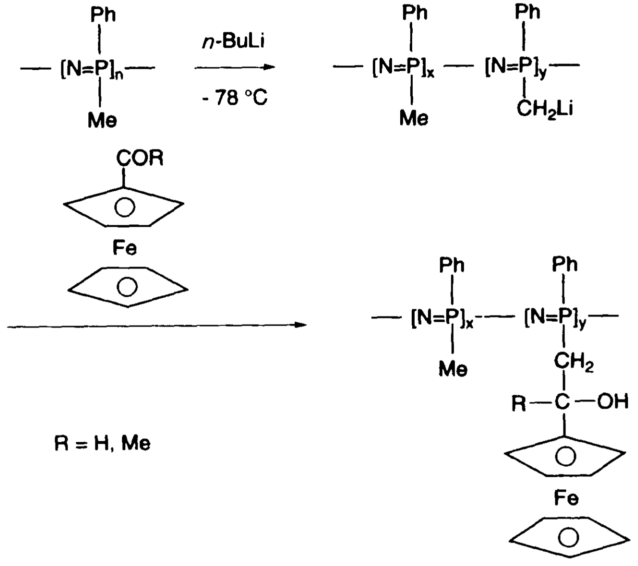
Recently, high molecular ferrocene polymers have been prepared by a ring opening polymerization as shown in eqs. (15.39)–(15.40) [96–97c].



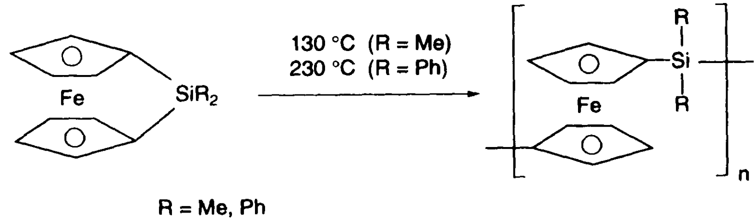
X	Molecular weight
Cl	13,700
Br	12,600
CN	44,300

AIBN = 2,2'-azobis-2-methylpropionitrile

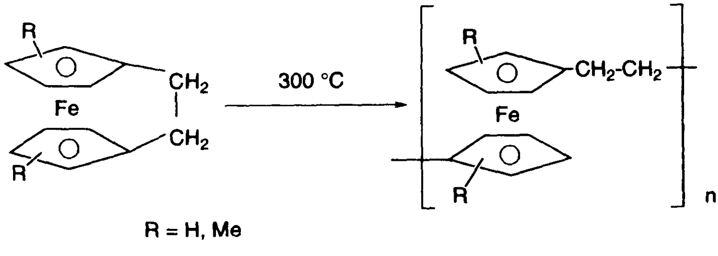
Scheme 15.9 [93].



(15.38)



(15.39)



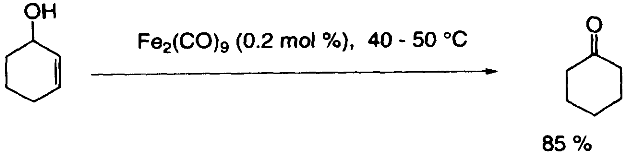
(15.40)

15.5.5 OTHERS

The reaction properties of organoiron compounds such as the isomerization (eq. (15.8)) and the reaction with protection of diene group (Scheme 15.8), have been used for organic syntheses [98,99]. Organoiron compounds are also used as various kinds of catalysts; for example, for the water-gas-shift reaction (eq. (15.41) [99,100]), syntheses of carbodiimide (eq. (15.42) [99]), isomerization of allylalcohol or allylether to ketone (eq. (15.43) [99]) and butadiene oligomerization [101], etc.

$$CO + H_2O \xrightarrow{Fe(CO)_5} CO_2 + H_2 \qquad (15.41)$$

$$2R{-}N{=}C{=}O \xrightarrow{Fe(CO)_5} R{-}N{=}C{=}N{-}R + CO_2 \qquad (15.42)$$



(15.43)

REFERENCES

[1] *Sekai Dai Hyakkajiten*, Heibonsha, Tokyo, vol. 19, p. 136, 1988.
[2] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
[3] *Kagaku Daijiten*, Tokyo Kagaku Doojin, Tokyo, p. 1480, 1989.
[4] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol. A14, p. 461, 1990.
[5] Kirk-Othmer, *Enclopedia of Chemical Technology*, 3rd ed., John Wiley, New York, vol. 13, p. 735, 1980.
[6] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, 4th ed., p. 831, 1987.
[7] K. Noack and M. Ruch, *J. Organomet. Chem.*, **17** (1969) 309.
[8] S.A. Miller, J.A. Tebboth and J.F. Tremaine, *J. Chem. Soc.*, (1952) 632.
[9] T.J. Kealy and P.L. Pauson, *Nature*, **168** (1951) 1039.
[10] R.B. King, *Organometallic Syntheses*, vol. 1, p. 73 (1965).
[11] R.B. King and J.J. Eisch, *Organometallic Syntheses*, vol. 3, p. 136 (1986).
[12] G.R. Knox, P.L. Pauson and D. Wilkinson, *J. Organomet. Chem.*, 450 (1993) 177.
[13] D.F. Shriver and K.H. Whitmire, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 4, p. 243, 1982.
[14] E.H. Braye and W. Hübel, *Inorg. Synth.*, **7** (1966) 178.
[15] *Jikken Kagaku Kouza 18, 4th ed.*, Japan Chemical Scoiety, Maruzen, Tokyo, p. 211, 1991.
[16] W. McFarlane and G. Wilkinson, *Inorg. Synth.*, **7** (1966) 181.
[17] R. Pettit and G.F. Emerson, *Adv. Organomet. Chem.*, **1** (1964) 1.
[18] J.E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83** (1961) 2954.
[19] B.M.R. Bandara, A.J. Birch and W.D. Raverty, *J. Chem. Soc., Perkin Trans. 1*, (1982) 1755.
[20] R.M.R. Bandara, A.J. Birch and B. Chauncy, *J. Organomet. Chem.*, **444** (1993) 137.
[21] R.B. King, *Organometallic Syntheses*, vol. 1, p. 128 (1965).
[22] H.D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45** (1962) 1927.

[23] M.D. Johnson, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 4, p. 331, 1982.

[24] R.B. King and M.B. Bisnette, *J. Organomet. Chem.*, **2** (1964) 15.

[25] E.G. Rochow, D.T. Hurd and R.N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley, New York, p. 244, 1957.

[26] Ch. Elschenbroich and A. Salzer, *Organometallic*, VCH, Weinheim, 1989.

[27] I. Omae, *Organomemtallic Intramolecular-coordination Compounds, J. Organometallic Chemistry Library 18*, Elsevier, Amsterdam, 1986.

[28] K. Jacob, W. Kretschmer, K.-H. Thiele, H. Gornitzka, F.T. Edelmann, I. Pavlik, A. Lycka and J. Holecek, *J. Organomet. Chem.*, **436** (1992) 231.

[29] D.W. Slocum, B.P. Koonsvitsky and C.R. Ernst, *J. Organomet. Chem.*, **38** (1972) 125.

[30] S.S. Crawford and H.D. Kaesz, *Inorg. Chem.*, **12** (1977) 3193.

[31] G. Wilkinson, *Org. Syntheses*, Col. Vol. 4, p. 476, 1963.

[32] J.F. Helling, S.L. Rice, D.M. Braitsch and R. Mayer, *J. Chem. Soc. Commun.* (1971) 930.

[33] J.F. Helling and D.M. Braitsch, *J. Am. Chem. Soc.*, **92** (1970) 7207.

[34] R.B. King, *Organometallic Syntheses*, vol. 1, p. 138 (1965).

[35] M. Aresta, P. Giannoccaro, M. Rossi and A. Sacco, *Inorg. Chim. Acta*, **5** (1971) 203.

[36] W.L. Jolly, *Inorg. Synth.*, vol. 11, p. 120, (1968).

[37] G. Wilkinson, M. Rosenblum, M.C. Whiting and R.B. Woodward, *J. Am. Chem. Soc.*, **74** (1952) 2125.

[38] P.F. Eiland and R. Pepinsky, *J. Am. Chem. Soc.*, **74** (1952) 4971.

[39] J.D. Dunits and L.E. Orgel, *Nature*, **171** (1953) 121.

[40] W. Pfab and E.O. Fischer, *Z. Anorg. Allg. Chem.*, **274** (1953) 316.

[41] F. Takusagawa and T.F. Koetzle, *Acta Cryst.*, **B35** (1979) 1074.

[42] D.P. Freyberg, J.L. Robbins, K.N. Raymond and J.C. Smart, *J. Am. Chem. Soc.*, **101** (1979) 892.

[43] B.T.M. Willis, *Acta Crystallogr.*, **13** (1960) 1088.

[44] R.K. Bohn and A. Haaland, *J. Organomet. Chem.*, **5** (1966) 470.

[45] Yu.T. Struchkov, V.G. Andrianov, T.N. Sal'nikova, I.R. Lyatifov and R.B. Materikova, *J. Organomet. Chem.*, **145** (1978) 213.

[46] A. Almenningen, A. Haaland, S. Samdal, J. Brunvoll, J.L. Robbins and J.C. Smart, *J. Organomet. Chem.*, **173** (1979) 293.

[47] M. Hisatome and K. Yamakawa, *Yuki Gosei Kagaku Kyokaishi*, **48** (1990) 319.

[47a] J. Watabe, M. Hisatome and K. Yamakawa, *Tetrahedron Lett.*, (1987) 1427.

[47b] M. Hisatome, J. Watanabe, K. Yamakawa, K. Kozawa and T. Uchida, *Bull. Chem. Soc. Japan*, **68** (1995) 635.

[48] M. Hisatome, J. Watanabe, K. Yamakawa and Y. Iitaka, *J. Am. Chem. Soc.*, **108** (1986) 1333.

[49] M. Hisatome, J. Watanabe, Y. Kawajiri and K. Yamakawa, *Organometallics*, **9** (1990) 497.

[50] M. Hisatome, K. Nakanishi, K. Yamakawa, K. Kozawa and T. Uchida, *Bull. Chem. Soc. Japan*, **65** (1995) 3275.

[51] K.L. Rinehart, Jr., R.J. Curby, Jr., D.H. Gustafson, K.G. Harrison, R.E. Gozak and D.E. Bublitz, *J. Am. Chem. Soc.*, **84** (1962) 3263.

[52] W. Finckh, B.-Z. Tang, D.A. Foucher, D.B. Zamble, R. Ziembinski, A. Lough and I. Manners, *Organometallics*, **12** (1993) 823.

[53] H. Stoeckli-Evans, A.G. Osborne and R.H. Whiteley, *Helv. Chim. Acta*, **59** (1976) 2402.

[54] H. Stoeckli-Evans, A.G. Osborne and R.H. Whiteley, *J. Organomet. Chem.*, **94** (1980) 91.

[55] A.G. Osborne, R.H. Whiteley and R.E. Meads, *J. Organomet. Chem.*, **193** (1980) 345.

[56] A.J. Deeming, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 4, p. 377, 1982.

[56a] C. Angelakos, D.B. Zamble, D.A. Foucher, A.J. Lough and I. Manners, *Inorg. Chem.*, **33** (1994) 1709.

[56b] D.A. Foucher, M. Edwards, R.A. Burrow, A.J. Lough and I. Manners, *Organometallics*, **13** (1994) 4959.

[57] S. Onaka, T. Moriya, S. Takagi, A. Mizuno and H. Furuta, *Bull. Chem. Soc. Japan*, **65** (1992) 1415.

[58] R. Broussier, A.D. Rold, B. Gautheron, Y. Dromzee and Y. Jeannin, *Inorg. Chem.*, **29** (1990) 1817.

[59] H. Schulz, K. Folting, J.C. Huffman, W.E. Streib and M.H. Chisholm, *Inorg. Chem.*, **32** (1993) 6056.

[60] S.A. Benyunes, L. Brandt, A. Fries, M. Green, M.F. Mahon and T.M.T. Papworth, *J. Chem. Soc. Dalton Trans.*, (1993) 3785.

[60a] T. Yoshida, S. Takaka, T. Adachi, T. Yoshida, K. Onitsuka and K. Sonogashira, *Angew. Chem. Int. Ed. Engl.*, **34** (1995) 319.

[60b] K. Onitsuka, T. Yoshida, A. Ichimura, T. Adachi, T. Yoshida and K. Sonogashira, *Chem. Lett.*, (1995) 427.

[60c] M. Viotte, B. Gautheron, M.M. Kubicki, Y. Mugnier and R.V. Parish, *Inorg. Chem.*, **34** (1995) 3465.

[60d] M.C. Gimeno, P.G. Jones, A. Lagura and C. Sarroca, *J. Chem. Soc. Dalton Trans.*, (1995) 1473.

[60e] N.J. Long, P.R. Raithby and P. Zanello, *J. Chem. Soc. Dalton Trans.*, (1995) 1245.

[60f] M. Sato, H. Shigeta, M. Sekino and S. Akabori, *J. Organomet. Chem.*, **458** (1993) 199.

[60g] C.P. Gallway and T.B. Rauchfuss, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 1319.

[61] O.S. Mills and G. Robinson, *Acta Crystallogr.*, **16** (1963) 758.

[62] S.G. Kukolich, M.A. Roehrig, D.W. Wallace and G.L. Henderson, *J. Am. Chem. Soc.*, **115** (1993) 2021.

[63] M.R. Churchill and R.F. See, *J. Organomet. Chem.*, **450** (1993) 171.

[64] G. Ferguson, J.F. Gallagher, C. Glidewell and C.M. Zakaria, *J. Chem. Soc. Dalton Trans.*, (1993) 3499.

[65] M. Mathew and G.J. Palenik, *Inorg. Chem.*, **11** (1972) 2809.

[66] J.F. Helling and D.M. Braitsch, *J. Am. Chem. Soc.*, **92** (1970) 7207.

[67] D. Astruc, E. Román E., J.E. Hamon and P. Batail, *J. Am. Chem. Soc.*, **101** (1979) 2240.

[68] A. Hills, D.L. Hughes, M. Jimenez-Tenorio, G.J. Leigh and A.T. Rowley, *J. Chem. Soc. Dalton Trans.*, (1993) 3041.

[69] Y. Ito, T. Konoike, T. Harada and T. Saegusa, *J. Am. Chem. Soc.*, **99** (1977) 1487.

[70] M. Buchmeiser and H. Scottenberger, *J. Organomet. Chem.*, **436** (1992) 223.

[71] M. Buchmeiser and H. Schottenberger, *J. Organomet. Chem.*, **441** (1992) 457.

[72] A.P. Bell and C.D. Hall, *J. Chem. Soc. Commun.*, (1980) 163.

[73] J.C. Medina, T.T. Goodnow, M.T. Rojas, J.L. Atwood, B.C. Lynn, A.E. Kaifer and G.W. Gokel, *J. Am. Chem. Soc.*, **114** (1992) 10583.

[74] P.D. Beer, D.B. Crowe, M.I. Ogden, M.G.B. Drew and B. Main, *J. Chem. Soc. Dalton Trans.*, (1993) 2107.

[75] R.A. Holwerda, J.S. Kim, T.W. Robison and R.A. Bartsch, *J. Organomet. Chem.*, **443** (1993) 123.

[76] J.C. Medina, I. Gay, Z. Chen, L. Echegoyen, G.W. Gokel, and B.P. Czech, *J. Am. Chem. Soc.*, **113** (1991) 365.

[77] H. Gornitzka, F.T. Edelmann and K. Jacob, *J. Organomet. Chem.*, **436** (1992) 325.

[78] A.J. Pearson, R.J. Shively, Jr., and R.A. Dubbert, *Organometallics*, **11** (1992) 4096.

[78a] A.T. Pearson and R.A. Dubbert, *Organometallics*, **13** (1994) 1656.

[79] L. Hill, C.J. Richards and S.E. Thomas, *Pure Appl. Chem.*, **62** (1990) 2057.

[80] L. Hill, C.J. Richards, S.P. Saberi and S.E. Thomas, *Pure Appl. Chem.*, **64** (1992) 371.

[81] L.S. Trifonov, A.S. Orahovats, R. Prewo and H. Heimgartner, *Helv. Chim. Acta*, **71** (1988) 551.

[82] W.A. Donaldson, P.T. Bell and M.-J. Jin, *J. Organomet. Chem.*, **441** (1992) 449.

[83] M. Franck-Neumann, M. Sedrati and M. Mokhi, *J. Organomet. Chem.*, **326** (1987) 389.

[84] S.S. Crawford, G. Firestein and H.D. Kaesz, *J. Organomet. Chem.*, **91** (1975) C57.

[85] D.W. Slocum, C.A. Jennings, T.R. Engelmann, B.W. Rockett and C.R. Hauser, *J. Org. Chem.*, **36** (1971) 377.

[86] H. Kisch and D. Garn, *J. Organomet. Chem.*, **409** (1991) 347.

[87] D. Garn, F. Knoch and H. Kisch, *J. Organomet. Chem.*, **444** (1993) 155.

[88] H. Gstach and H. Kisch, *Z. Naturforsch.*, **B38** (1983) 251.

[89] N. Hagiwara and M. Nakamura ed., *Organometallic Polymer*, Gakkai Shuppan Center, Tokyo, 1982.

[90] M.H. George and G.F. Hayes, *J. Polym. Sci. Polymer. Ed.*, **13** (1975) 1049.

[91] Y. Sasaki, L.L. Walker, E.L. Hurst and C.U. Pittman, Jr., *J. Polymer. Sci., Polymer Ed.*, **11** (1973) 1213.

[92] C.U. Pittman, Jr., and Y. Sasaki, *Chem. Lett.*, (1975) 383.

[93] S. Afeworki, P.K. Baker, O.L. Parri and C. D'Silva, *J. Organomet. Chem.*, **431** (1992) 81.

[94] P. Wisian-Neilson and R.R. Ford, *Macromolecules*, **22** (1989) 72.

[95] A.L. Crumbliss, D. Cooke, J. Castillo and P. Wisian-Neilson, *Inorg. Chem.*, **32** (1993) 6088.

[96] D.A. Foucher, B.-Z. Tang and I. Manners, *J. Am. Chem. Soc.*, **114** (1992) 6246.

[97] J.M. Nelson, H. Rengel and I. Manners, *J. Am. Chem. Soc.*, **115** (1993) 7035.

[97a] I. Manners, *Adv. Organomet. Chem.*, **37** (1995) 131.

[97b] R. Rulkens, A.J. Lough and I. Manners, *J. Am. Chem. Soc.*, **116** (1994) 797.

[97c] R. Rulkens, Y. Ni and I. Manners, *J. Am. Chem. Soc.*, **116** (1994) 12121.

[98] A.J. Pearson, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 8, p. 939, 1982.

[99] J. Tsuji, *Yukigosei okaeta Sen-i-kinzoku*, Kagaku Dojin, Tokyo, 1991.

[100] L.S. Sunderlin and R.R. Squires, *J. Am. Chem. Soc.*, **115** (1993) 337.

[101] A. Carbonaro and A. Grecio, *J. Organomet. Chem.*, **25** (1970) 477.

16 Organoruthenium Compounds

16.1 INTRODUCTION

As ruthenium is not a precious metal such as platinum and palladium, and is not as much used a metal for alloy components such as nickel and cobalt, ruthenium is generally not a well known metal, but it is also little known as a catalyst.

As for organoruthenium compounds, they have been published for their catalytic reactions. Recently, many studies of organosynthetic reactions have been reported.

16.2 RUTHENIUM

Ruthenium is an element of group 8 of the periodic table. It exists as 0.001 ppm in the Earth's crust, at a similar level to Ag (0.07 ppm) and Au (0.0011 ppm). Ruthenium has only been produced in quantities of a few tons per year [1–3].

Ruthenium is produced mainly from an anode slime yielded when crude copper or crude nickel, obtained from nickel sulfide ores, is electrolytically refined. The anode slime contains precious metal elements. It is treated with hot aqua regia and platinum, palladium and gold are separated as their chloro complexes. Then, by nitric acid treatment, fusion treatment with $NaHSO_4$, and fusion treatment with Na_2O_2, silver, rhodium and iridium are separated. The residual ruthenium and osmium salts are dissolved in water, and the osmium is separated by treatment with chlorine, hydrochloric acid and nitric acid. The ruthenium salt is treated with ammonium chloride to afford a ruthenium salt ($(NH_4)_3RuCl_6$), and the reduction with hydrogen yields ruthenium powder [1,4–6].

Ruthenium is a silver white, hard, fragile metal, it tends to become powder and the color of the powder is grayish black. Properties of ruthenium are shown in Table 16.1 [1,6,7].

Ruthenium has a high corrosion resistance and aqua regia, sulfuric acid and hydrochloric acid cannot attack ruthenium at 100 °C. But it is slightly attacked by chlorine water and bromine water at room temperature. It is slowly oxidized at 450 °C or higher in air to yield RuO_2 [5]. The treatment with chlorine or bromine on an alkaline ruthenium salt gives RuO_4. RuO_4 is volatile and explosive [1]. Ruthenium is heated with chlorine or iodine to afford the trihalides [1].

Ruthenium is used as an alloy component since it increases the hardness of platinum or palladium without lowering the corrosion resistance [4,5]. The alloy containing 30–70% ruthenium is used as an electric contact, the penpoint of a

Table 16.1 Properties of ruthenium [1,6,7]

Property	Value
melting point, °C	2310
boiling point, °C	3900
crystal structure	hexagonal
density, 20 °C, g/cm^3	12.45
specific heat at 0 °C, J g^{-1}	0.2306
linear coefficient of thermal expansion at 20 °C, K^{-1}	9.1×10^{-6}
electrical resistivity at 20 °C, $\mu\Omega$·cm	7.4
hardness	
Mohs scale	6.5
Vickers hardness, annealed	220
thermal conductivity at 27 °C, Wm^{-1}K^{-1}	117
mass susceptibility, cm^{3}g^{-1}	0.43×10^{-6}

fountain pen and the axis of instruments for which abrasion resistance and corrosion resistance are required [5].

Ruthenium and ruthenium compounds are mainly used as hydrogenation catalysts and oxidation catalysts, e.g., catalysts for the hydrogenation reaction of carbon monoxide and aromatic compounds, aldehyde synthesis by fission of a carbon–carbon double bond, from alcohols to aldehydes or ketones, aldehydes to carboxylic acids, and ester synthesis from ether [5–7].

The other uses as catalysts are for synthesis of ammonia, methylation of carbon monoxide or carbon dioxide, steam reforming of naphtha and LPG, decomposition of peroxide, and treatment of waste water, etc. Market prices of precious metals are shown in Table 16.2 [3]. Ruthenium has a low price compared to a precious metal.

Table 16.2 Market price of precious metals [3] (yen/g) (May 26, 1994)

Platinum	1400
Palladium	480
Rhodium	2500
Ruthenium	80

16.3 PREPARATION OF ORGANORUTHENIUM COMPOUNDS

Organoruthenium compounds are prepared by the following five reaction methods.

(1) Carbonylations

(2) Reactions with unsaturated hydrocarbons
(3) Reactions with rutheniumcarbonyl compounds
(4) Reactions with ruthenocene derivatives
(5) Others

16.3.1 CARBONYLATIONS

Ruthenium chloride reacts easily with carbon monoxide under pressure to afford ruthenium carbonyl compounds. The product is recrystallized in hexane to yield a yellow crystal in 74% yield. The total yield is 85–95% by using the mother liquors repeatedly [8]. The $Ru_3(CO)_{12}$ obtained decomposed at its melting point in air, ignites violently and is stable up to 231 °C in argon. It dissolves in most solvents except for petroleum ether and alcohol [8,9].

$$3RuCl_3{\bullet}3H_2O \quad + \quad 12CO \xrightarrow[\text{in MeOH}]{\text{50 - 65 atm, 125 °C, 8h}} Ru_3(CO)_{12} \qquad (16.1)$$

orange crystal, 74 %
mp 155 °C, dp 231 °C

In the previous chapter $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are described as ironcarbonyl compounds. Ruthenium also forms $Ru(CO)_5$ and $Ru_2(CO)_9$ besides $Ru_3(CO)_{12}$. $Fe(CO)_5$ is the most stable of the iron carbonyls and is used as a basic compound. But in ruthenium, $Ru_3(CO)_{12}$ is the most stable compound.

$Ru(CO)_5$ is prepared by the direct reaction of ruthenium metal with carbon monoxide as shown in eq. (16.2) [9]. $Ru(CO)_5$ is also prepared in high yield by reaction of ruthenium acetylacetonate complex with a mixture gas of CO/H_2 (2 : 1) in heptane [9,10].

$$Ru \quad + \quad CO \xrightarrow{\text{200 atm, 180 °C}} Ru(CO)_5 \qquad (16.2)$$

$$\underset{}{Ru(acac)_3} \quad + \quad \underset{2\,:\,1}{CO/H_2} \xrightarrow[\text{in heptane}]{\text{200 atm, 180 °C, 8 h}} \underset{51.1\ \%}{Ru(CO)_5} \qquad (16.3)$$

$Ru(CO)_5$ is a colorless volatile liquid. By heating at 50 °C or more or by light irradiation, $Ru(CO)_5$ releases carbon monoxide immediately to yield $Ru_3(CO)_{12}$ [9]. In contrast, $Ru_3(CO)_{12}$ reacts with carbon monoxide at 100 °C under 133 atm. to afford $Ru(CO)_5$ almost quantitatively [8,11]. $Ru_2(CO)_9$ is prepared by the UV irradiation of $Ru(CO)_5$ in heptane at -40 °C. $Ru_2(CO)_9$ is stable at low temperatures, but at room temperature, it rapidly releases carbon monoxide to afford $Ru_3(CO)_{12}$ [9,11].

$$Ru(CO)_5 \xrightarrow[\text{in heptane}]{\text{UV, -40 °C}} Ru_2(CO)_9 \qquad (16.4)$$

If the carbonylation of $RuCl_3$ shown in eq. (16.1) is carried out under mild reaction conditions, the dimer holding chlorine of ruthenium chloride is yielded as shown in eq. (16.5) [9,12]. The dimer is also produced by a reaction with formic

$$RuCl_3{\bullet}xH_2O \quad + \quad CO \xrightarrow[\text{in methanol}]{\text{10 - 17 atm, 65 °C, 0.5 h}} \underset{71\ \%}{[RuCl_2(CO)_3]_2} \qquad (16.5)$$

acid and hydrochloric acid as shown in eq. (16.6) [9,13]. The dimer forms the bridged structure of the chlorine atoms. If formaldehyde is used as a carbonylation

$$RuCl_3 \quad + \quad HCOOH/HCl \xrightarrow{\text{reflux, 24 h}} \underset{77\ \%}{[RuCl_2(CO)_3]_2} \qquad (16.6)$$

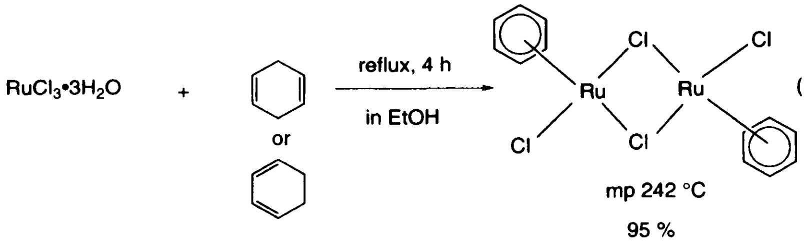
reagent, the reaction proceeds with both carbonylation and hydrogenation. For example, ruthenium chloride reacts with formaldehyde in the presence of phosphine to afford the carbonylphosphinehydride in high yield as shown in eq. (16.7) [8,14].

$$RuCl_3{\bullet}xH_2O \quad + 3PPh_3 \quad + \quad HCHO \xrightarrow[\text{in 2-methoxyethanol}]{\text{reflux, 10 min}} \underset{\substack{\text{mp 209 -210 °C} \\ 93\ \%}}{RuClH(CO)(PPh_3)_3} \qquad (16.7)$$

16.3.2 REACTIONS WITH UNSATURATED HYDROCARBONS

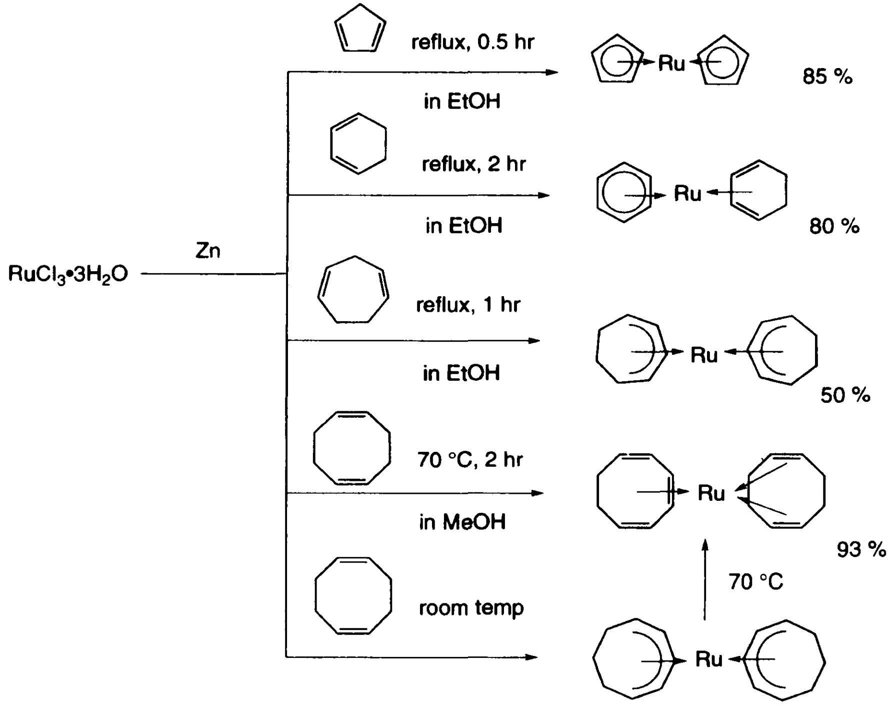
Organoruthenium compounds tend to form complexes coordinated by the 10 electrons of cyclic unsaturated compounds similar to ferrocene in organoiron compounds, for example, ruthenocene $(\eta^5\text{-}C_5H_5)_2Ru$ and $(\eta^6\text{-}C_6H_6)$ $(\eta^4\text{-}C_6H_8)Ru$. As shown in Scheme 16.1, ruthenium chloride$\cdot 3H_2O$ reacts with unsaturated cyclic compounds in the presence of zinc metal to afford cyclic compounds coordinated by 10 electrons by dehydrogenation [15–18]. In the case of cyclopentadiene, ruthenocene is formed by the coordination of two five-electron rings. In the case of 1,3-cyclohexadiene, the complex is obtained to be coordinated with 4-electron 1,3-cyclohexadiene and with 6-electron benzene. In the case of 1,3-cycloheptadiene and 1,5-cyclooctadiene, similarly all of the products are coordinated by a total of 10 electrons [15,16].

If ruthenium chloride reacts with 1,3-cyclohexadiene or 1,4-cyclohexadiene in the absence of zinc powder, cyclohexadiene is dehydrogenated to benzene, and the dimer of a chloro-bridged benzene complex is obtained [8,19,20]. The dimer is easily substituted to afford the replacement compound by heating with a compound having a higher coordination reactivity than benzene, such as *p*-cymene (MeC_6H_4-*i*-Pr) and then with C_6Me_6 as shown in eq. (16.9) [20].



(16.8)

$$[(\eta^6\text{-}C_6H_6)RuCl_2]_2 \xrightarrow{p\text{-cymene}} \underset{80\ \%}{[(\eta^6\text{-}MeC_6H_4\text{-i-Pr})RuCl_2]_2} \xrightarrow{C_6Me_6} [(\eta^6\text{-}C_6Me_6)RuCl_2]_2 \qquad (16.9)$$



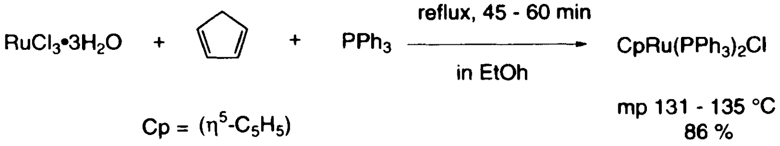
Scheme 16.1 [8,15–18]

The dimer reacts with pyridine or phosphine to afford the monomer by fission of the bridge bond as shown in eq. (16.10) [8,19,20].

$$[(\eta^6\text{-}C_6H_6)RuCl_2]_2 \xrightarrow{\quad L \quad} (\eta^6\text{-}C_6H_6)RuCl_2L \qquad (16.10)$$

L - pyridine, t-phoshines, t-arsines

Ruthenium chloride reacts with cyclopentadiene and phosphine to afford the monomer similar to the above compounds as shown in eq. (16.11) [8,21]. This diphosphine compounds are used as raw materials for other derivatives by replacement of the chlorine or phosphine moiety (see Scheme 16.4) [21].



(16.11)

16.3.3 REACTIONS WITH RUTHENIUMCARBONYL COMPOUNDS

$Ru_3(CO)_{12}$ is the most stable and so the handling is easy. Then $Ru_3(CO)_{12}$ is used as the basic compound for the raw materials of organoruthenium compounds. For example, the hydride is prepared by the reaction of $Ru_3(CO)_{12}$ with bubbling hydrogen into the octane solution and refluxing for one hour as shown in eq. (16.12)

$$4Ru_3(CO)_{12} + 6H_2 \xrightarrow[\text{in octane}]{\text{reflux, 1 h}} 3Ru_4(\mu\text{-H})_4(CO)_{12} + 12CO \qquad (16.12)$$

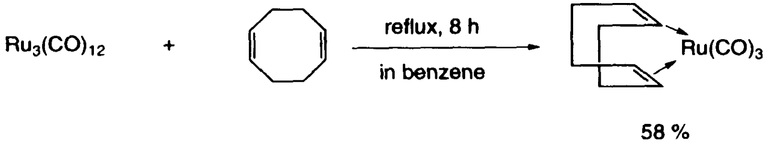
80 %

[8,22]. Chloroform is used as a mild chlorination agent. $Ru_3(CO)_{12}$ reacts with chloroform in the presence of ethanol which acts as a stabilizer to afford the dimer as shown in eq. (16.13) [8].

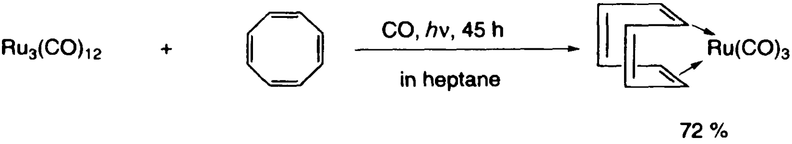
$$2Ru_3(CO)_{12} + 4CHCl_3 \xrightarrow{N_2,\ 5\ \text{atm},\ 110\ ^\circ C,\ 6\ -\ 8\ h} 3[Ru(CO)_2Cl_2]_2 \qquad (16.13)$$

53 - 60 %

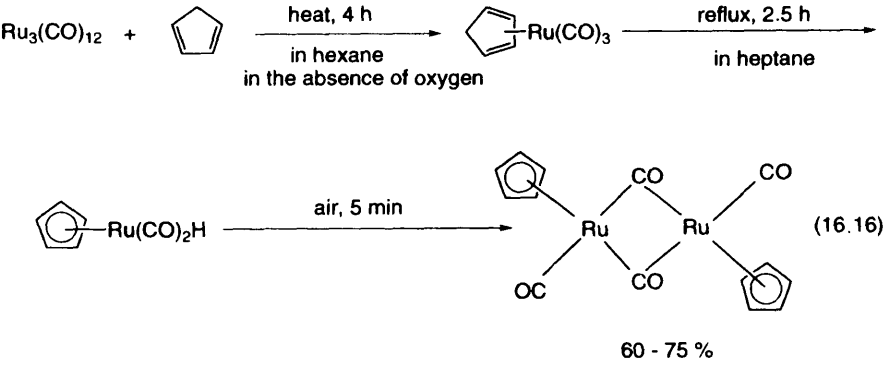
$Ru_3(CO)_{12}$ reacts with cyclooctadiene or cyclooctatetraene to afford the ring compounds coordinated by four electrons as shown in eqs. (16.14) and (16.15) [8,23]. However, in the reaction with cyclopentadiene, since the four-electron coordination compound is liable, it is easily dehydrogenated with bubbling air and the stable dimer readily yields as shown in eq. (16.16) [8,24].



(16.14)



(16.15)



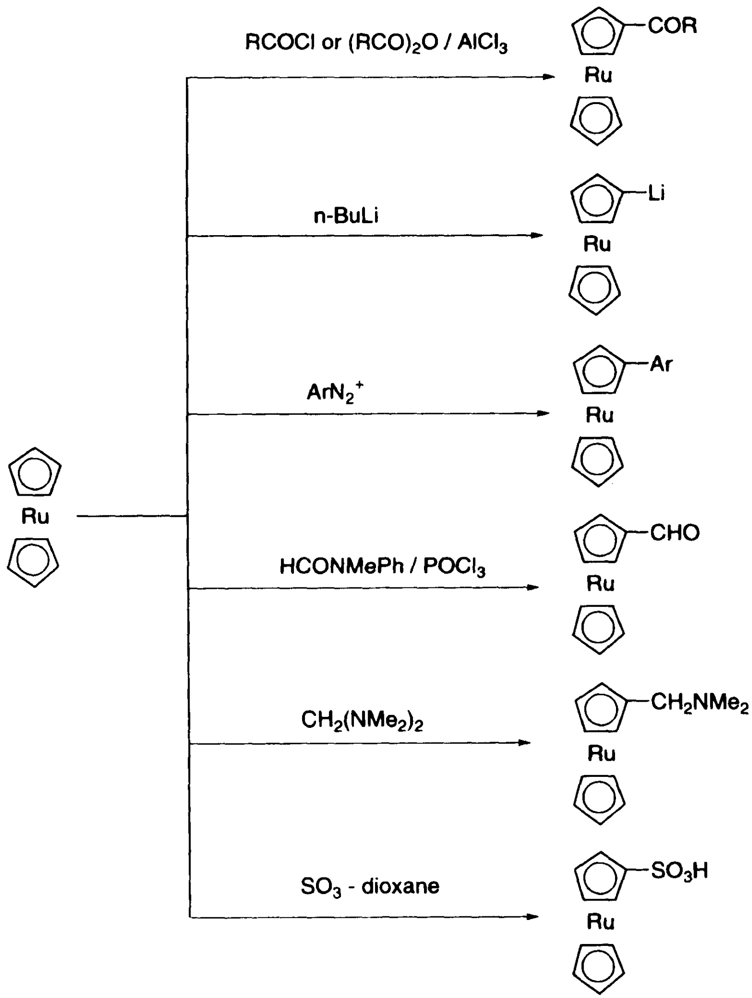
(16.16)

16.3.4 REACTIONS WITH RUTHENOCENE DERIVATIVES

Ruthenocene is easily synthesized by the reaction of ruthenium chloride with cyclopentadiene as shown in Scheme 16.1. Ruthenocene is a cream-colored crystal of mp 199–201 °C, stable similar to ferrocene, and it decomposed at ca. 610 °C. It is heated at 600 °C under hydrogen atmosphere to yield highly pure filmy ruthenium metal. It is stable to chlorine, hydrogen chloride and sulfuric acid in the absence of oxygen [17].

Ruthenocene has aromatic properties similar to ferrocene and its electrophilic substitution reactions are liable to proceed. For example, a Friedel–Crafts acylation, metalation, arylation, formylation, a Mannich reaction and sulfonation all readily proceed as shown in Scheme 16.2 [17].

The electrophilicity of ruthenocene also increases with the coordination of the metal atom. However, the effect is not so large as in ferrocene. Electronegativities of metalocenes are ferrocene: 2.08, and ruthenocene: 2.27. The acidity of ruthen-

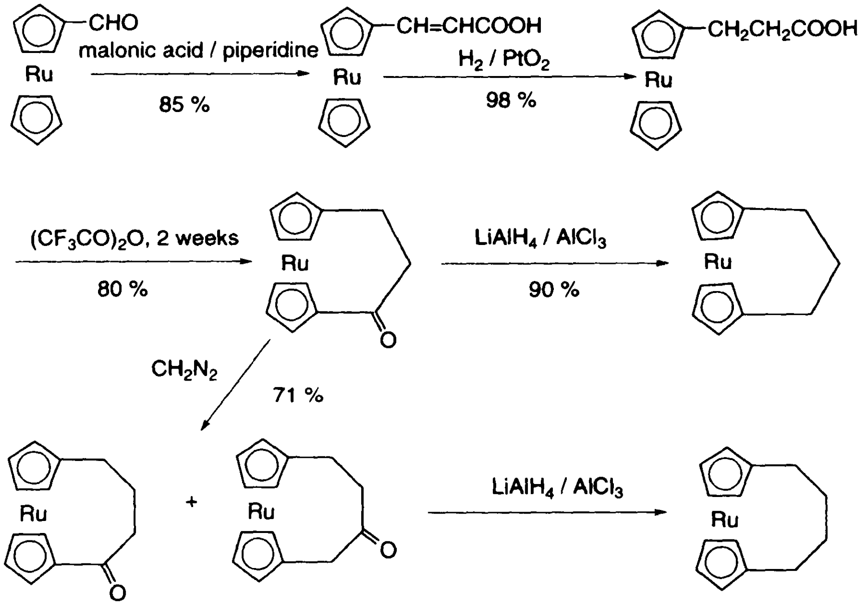


Scheme 16.2 [17]

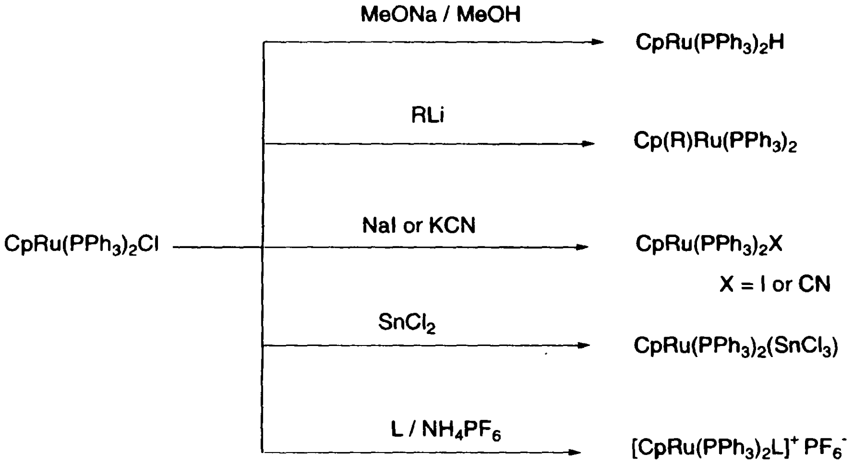
ocene carboxylic acid (RcCOOH) is 1.4 times weaker than that of benzoic acid, and 1.7 times stronger than that of ferrocene carboxylic acid (FcCOOH) [17].

Ruthenocene easily forms the bridge structure of ruthenocephane in high yield as shown in Scheme 16.3 [17].

Monocyclopentadienylruthenium, to which one cyclopentadienyl ring bonds, is prepared not from ruthenocene but from $RuCl_3{\cdot}3H_2O$ or $Ru_3(CO)_{12}$, since ruthenocene is very stable. In particular, $CpRu(PPh_3)_2Cl$ shown in eq. (16.11) is used as the raw material for monocyclopentadienyl derivatives as shown in Scheme 16.4 [17].



Scheme 16.3 [17]

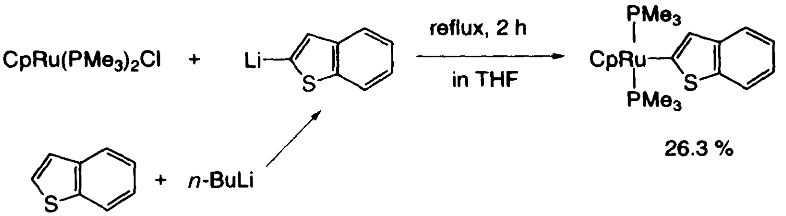


L = MeOH, RCN, RNC, CO, PR$_3$, P(OR)$_3$, etc.

Scheme 16.4 [17]

16.3.5 OTHERS

As the other synthetic method of organoruthenium compounds, the reaction of organolithium compounds or Grignard reagents with metal halides, which is the representative synthetic method of the main group organometallic compounds, is also available [25–28]. For example, organoalkali metal compounds react easily with ruthenium halides to form condensation products as shown in eq. (16.17) [25].

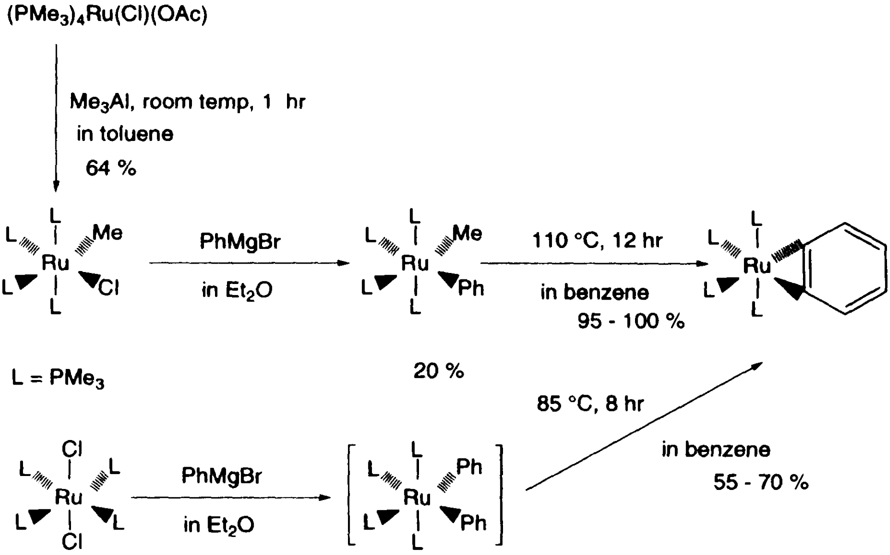


(16.17)

As the reaction with organomagnesium compounds, Grignard phenyl reagents react with ruthenium halides to afford phenylruthenium compounds, and the phenylruthenium compounds are heated to afford a benzyne ruthenium as shown in Scheme 16.5 [28].

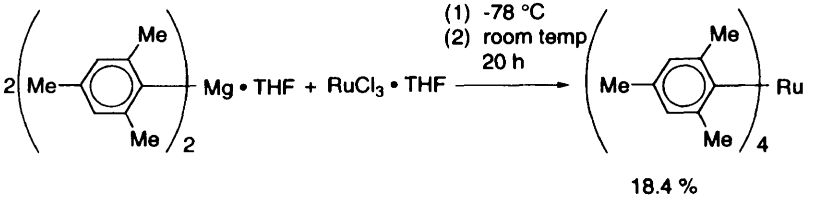
As shown in eq. (16.18), diarylmagnesium reacts with ruthenium chloride to afford a tetraarylruthenium compound [26].

Metal hydrides are prepared by the reaction of ruthenium chloride with a reducing agent such as $NaBH_4$. For example, dichlorotris(triphenylphosphine)-



Scheme 16.5 [28]

ruthenium reacts with $NaBH_4$ to afford the tetrahydride in high yield as shown in eq. (16.19) [8].



(16.18)

$$\mathrm{Ru(PPh_3)_3Cl_2} \quad + \quad \mathrm{4NaBH_4} \xrightarrow[\text{in EtOH}]{\qquad\qquad} \mathrm{Ru(PPh_3)H_4} \qquad (16.19)$$

mp 130 °C
90 %

Ruthenium chloride reacts with a carboxylic acid in the presence of potassium hydroxide to afford the carboxylic acid salt hydride in a high yield as shown in eq. (16.20) [8,29].

$$\mathrm{RuCl_3{\bullet}3H_2O} + \mathrm{3PPh_3} + \mathrm{CH_3COOH} + \mathrm{3KOH} \xrightarrow[\text{in EtOH}]{\text{reflux, 10 min}}$$

$$\mathrm{Ru(H)(OCOCH_3)(PPh_3)_3} + \mathrm{3KCl} \qquad (16.20)$$

mp 220 -223 °C
80 %

16.4 STRUCTURE OF ORGANORUTHENIUM COMPOUNDS

As ruthenium is in the same group as iron, it is liable to form compounds satisfying the 18-electron rule by coordination with 10 electrons. Ruthenocene, corresponding to ferrocene of organoiron compounds, is coordinated with 10 electrons. Ferrocene is liable to form the staggered structure described in the previous chapter, but ruthenocene forms an eclipsed structure as shown in Figure 16.1 [17,30]. Further, decabromonoruthenocene ($(\eta^5\text{-}C_5Br_5)_2Ru$) is substituted by bromine [31], and 2,5-dimethylruthenocene [32] also forms the eclipsed structures.

Ruthenocene also forms the bridge structure of two cyclopentadienyl rings: the chain element is not only a carbon chain (Scheme 16.3) but also silicon, phosphorus and palladium atom [32a,32b].

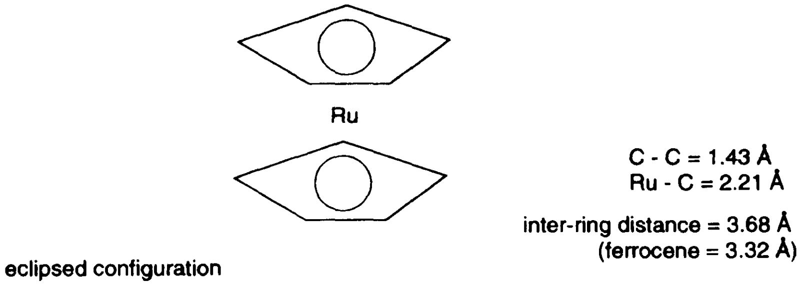


Figure 16.1 Crystal structure of ruthenocene [17,30].

As shown in Figure 16.2, the compound coordinated with 11 electron of η^5 and η^6, is liable to form Ru^+ and the compound coordinated 12 electron η^6 and η^6 is liable to form R^{2+} [33–38].

Pentamethylruthenocene (Cp*RuCp, Cp* $= \eta^5$-C_5Me_5, Cp $= \eta^5$-C_5H_5) reacts with $(Cp^*Ru(OMe)_2]_2/CF_3SO_3$ to afford a triple-decker ruthenocene as shown in Figure 16.3 [39].

Borabenzene (C_5H_5BR type) is liable to form a triple-decker compound as shown in organoiron compounds in the previous chapter, the similar organoruthenium compounds are also obtained as $[Cp^*RuC_5H_5BMeRuCp^*]^+$ [40]. A tetra-decker-sandwich compound containing cobalt is also prepared [41].

As the ruthenocene forms a structure in which the ruthenium atom is placed between two cyclopentadienyl rings and is called a sandwich structure. If only one cyclopentadienyl ring bonds to ruthenium, it is called a halfsandwich structure.

If one cyclopentadienyl ring bonds to ruthenium, the total number of electrons coordinated by the residual ligand groups is five. The residual ligand are two types of three ligands and four ligands. As these structures resemble a piano-stool structure, these are called a three-legged piano-stool structure and a four-legged

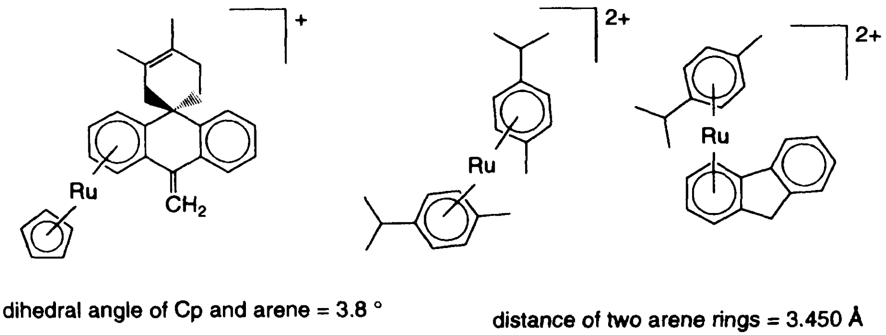


Figure 16.2 Structures of mocationic η^5,η^6-Ru^+; complex and dicationic η^6,η^6-Ru^{2+}; complexes [34–36].

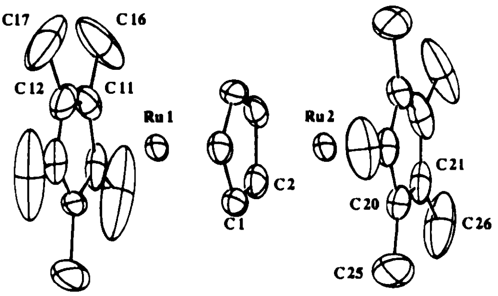


Figure 16.3 Structure of the cation of triple-decker salt $[Cp^*Ru(\mu\text{-}Cp)RuCp^*]^+$ [39].

piano-stool structure, respectively. For example, $CpRu(PPh_3)_2Cl$ (eq. (16.11) forms the three-legged piano-stool structure, if the coordination of a cyclopentadienyl ring is thought to be a three coordination. This structure is a distorted octahedral structure. If the coordination of the cyclopentadienyl ring is thought to be a one coordination, this structure is a distorted tetrahedral structure [42].

$CpRu(PPh_3)_2Cl$ has a piano-stool structure of which the general formula is $CpRu(PPh_3)_2X$ and the other examples are $CpRu(PMe_3)_2Cl$ [42], $CpRu(PPh_3)_2H$ [43], $CpRu(PPh_3)_2[C{\equiv}C\text{-}C(OCOCF_3){=}CMe_2)$ [44], $CpRu(PPhMe_2)_2({=}C{=}CH_2)$ [45] and $CpRu(PMe_3)_2(C{\equiv}C\text{-}ZrCp_2Cl)$ [46]. These structures are determined by X-ray diffraction studies.

$\eta^5\text{-}C_5Me_5$ is abbreviated as Cp* and the other piano-stool structure containing Cp or Cp* are $Cp^*Ru(CH_2Cl)_2NO$ [47], $CpRu(PPh_3)(CO)SS(O)CHMe_2$ [48], $Cp^*Ru(SOMe_2)_2Cl$ [49], $[CpRu(CH_3CN)_3]^+$ [50], $[CpRu(CH_3CN)_2Cl]^+$ [51], $CpRu{=}C(Ph)C_6H_4CH_2(CO)$ [52], $CpRu(PPh_3)(CH_2CH_2CH_2CH_2)$ [53], and $(MeC_5H_5)Ru(BINAP)Cl$ (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) [54]. These are three-legged piano-stool structures and examples of the four-legged piano-stool structure are $CpRu(PH_3)H_3$ [55], $CpRu(PH_3)_2H_2$ [55], and $Cp^*Ru(CH_2CHMeP(i\text{-}Pr)_2(H)SiMePh_2$ [27], etc.

The compounds are coordinated with an η^6-benzene ring and are liable to bond the four-electron ligand. For example, as shown in Figure 16.5, the coordination compounds of a benzene ring with a diene is formed [56]. Similarly the complex of

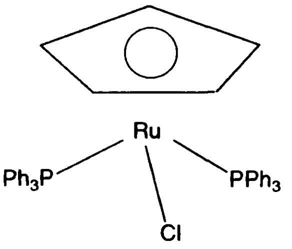


Figure 16.4 Three-legged piano-stool structure of $CpRu(PPh_3)_2Cl$ [42].

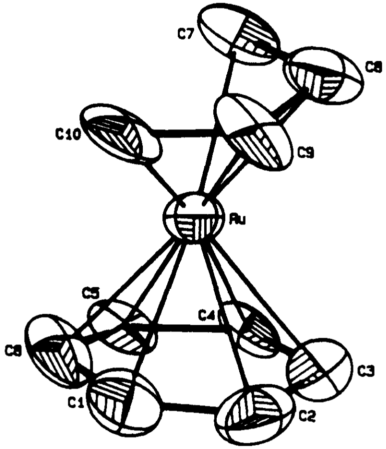


Figure 16.5 Structure of (η^6-benzene)(η^4-but-1,3-diene)rutheniumm [56].

C_6Me_6 with cyclopentadienyl ring containing a sulfur atom also forms a η^6 and η^4 complex [57].

The halfsandwich structure of a benzene ring also forms piano-stool structures as shown in Figure 16.6. However, the leg of the stool is four-electron coordination by one electron less than the cyclopentadienyl complexes [58].

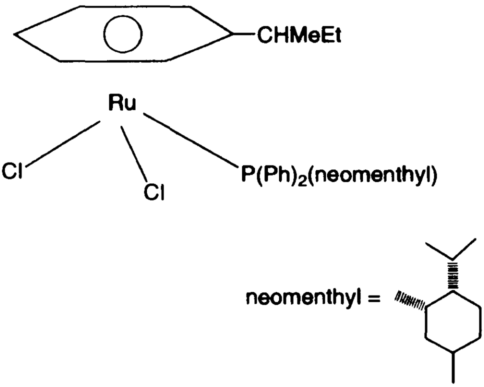
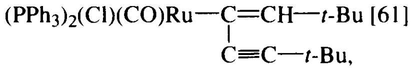


Figure 16.6 Piano-stool structure of (η^6-$C_6H_5CHMeEt$)$RuP(Ph)_2$(neomenthyl) [58].

Organoruthenium compounds form tetrahedral, trigonal bipyramidal and octahedral structure of four, five and six-coordination, respectively. An example of a tetrahedral structure is $(1,3,5\text{-}C_6H_2(Me)_3)_4Ru$ [36], those of trigonal bipyramidal are (o-tolyl)$RuCl(CO)(PPh_3)_2$ [59], $Ru(CO)_4(P(OMe)_3)$ [60] and



$$(PPh_3)_2(Cl)(CO)Ru{-}\underset{\displaystyle C{\equiv}C{-}t\text{-}Bu,}{\underset{|}{C}}{=}CH{-}t\text{-}Bu\ [61]$$

and that of an octahedral structure is $(PPh_3)_2Ru(I)(CO)(CN\text{-}p\text{-tolyl})(SnMe_2SH)$ [62], $[RuBr_2(CO)_3]_2$ [63,64], etc.

Benzyne complexes shown in Scheme 16.5 form a similar octahedral structure as shown in Figure 16.7. The bond length of C≡C of benzyne is 1.3555 Å, it is shorter than the other C=C bonds (1.372 Å–1.411 Å). The benzyne complex is a white solid, very liable to air, but it is stable for several months at room temperature under an inert gas atmosphere. It reacts with water at 20 °C and the π-coordination changes to two σ-bonds of phenyl and OH bond [28]. Ruthenium phosphine reacts with *t*-butylacetylene to afford a ruthenium carbene ($Br_2(PPh_3)_2Rn{=}C{=}CH(t\text{-}Bu)$) via an acetylene-$\pi$-complex as shown in Figure 16.7.

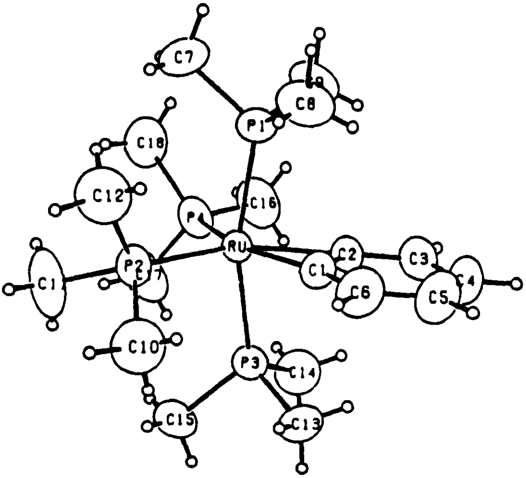


Figure 16.7 Structure of ruthenium benzyne complex ($(\eta^2\text{-}C_6H_4)Ru(PMe_3)_4$) [28].

(p-Tolyl)Ru(Cl)(CO)$(PPh_3)_2$ as shown in Figure 16.8 is a square pyramidal structure of five-coordination. However, the distances of two hydrogen in benzene rings is 2.73 Å and 2.91 Å to Ru. These lengths are longer than Ru-H of ruthenium hydride and are almost the same as the other agostic bond of Ru-H. These bonds are considered to be agostic bonds. Then this structure may be of an octahedral structure [59–59b].

Ruthenium is liable to form a variety of clusters. The cluster is an atom group to form a polyhedron in which three or more atoms directly bond. The atoms are nonmetal elements such as C, S and P and metal elements such as B, Pb, Fe, Co, Rh and Pt.

$Ru_3(CO)_{12}$ is yielded when $Ru(CO)_5$ is heated as described above. As shown in Figure 16.9, $Ru_3(CO)_{12}$ is thought to be a simple cluster [65,66]. The average distance of Ru-C(O) at the axial position is 1.942 Å which is slightly longer than

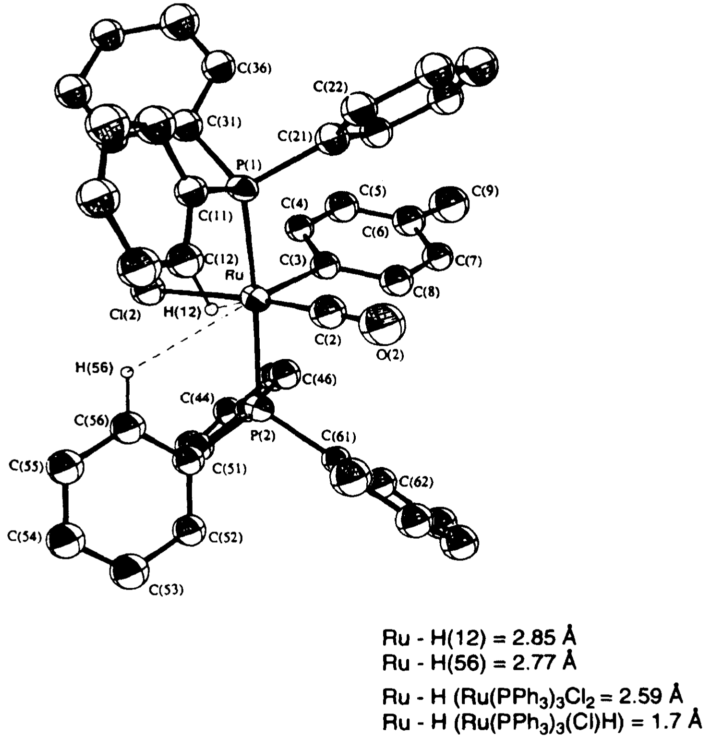


Figure 16.8 Structure of (p-Tolyl)Ru(Cl)(CO)$(PPh_3)_2$ [59–59b].

that at the equatorial position, which is 1.921 Å. It slightly tilts by the repulsion of van der Waals force [65].

16.5 REACTIONS OF ORGANORUTHENIUM COMPOUNDS

Ruthenium is used as a catalyst, especially for reduction, oxidation and addition [17,66a,66b]. As organoruthenium compounds are reactive to a cyclopentadienyl ring or benzene ring, the formation reactions of these aromatic rings are liable to proceed. Cyclometalation as the other reaction is also liable to proceed.

16.5.1 REDUCTIONS

The ruthenium catalysts for reduction are phosphine catalysts such as $RuCl_2(PPh_3)_3$ and $RuH_2(PPh_3)_4$. Optically active phosphine complexes are used for asymmetric hydrogenation reactions. Formic acid, alcohol and hypophosphorous acid ammonium, besides hydrogen, are used as the hydrogen source [66a–68]. For example, in the reaction shown in eq. (16.21), $RuCl_2(PPh_3)_3$ is used as the catalyst and formic acid is used for the hydrogen source [69].

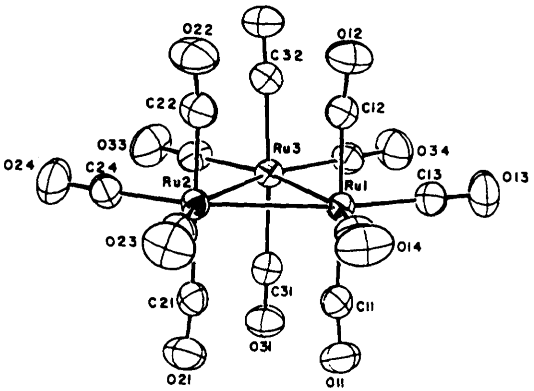
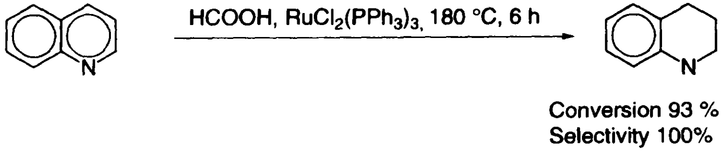
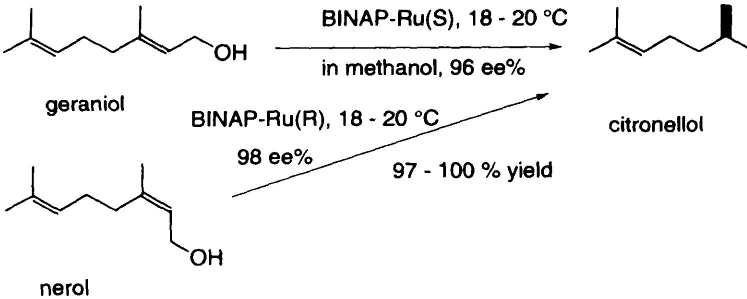


Figure 16.9 Structure of triruthenium dodecacarbonyl, $Ru_3(CO)_{12}$ [65].

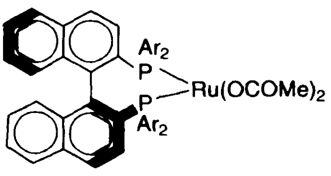


(16.21)

In the reaction shown in eq. (16.22), optically active 2,2′-bis(diarylphosphino)-1,1′-binaphthyl complex is used as a catalyst, methanol is used as the hydrogen source, and highly optical pure citronellol is obtained in high yield [70].

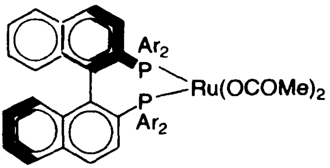


(16.22)



Ar = p-MeC_6H_4

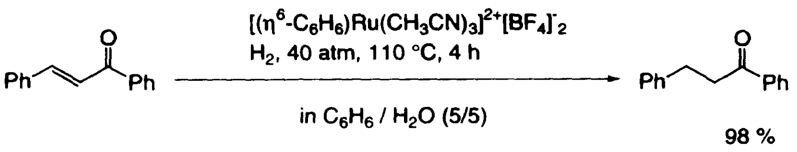
BINAP-Ru(S)



Ar = Ph

BINAP-Ru(R)

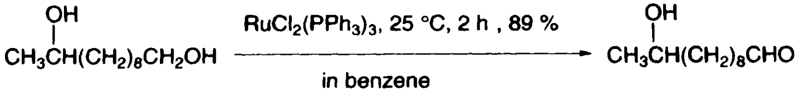
A benzene complex is used besides phosphine complexes as the ruthenium catalyst as shown in eq. (16.23). In this reaction, the use of the mixed solvent of water and benzene improves the yield very much. The water is not a simple solvent since it is found by using a D_2O–benzene solvent that it acts as a base to ruthenium [71].



(16.23)

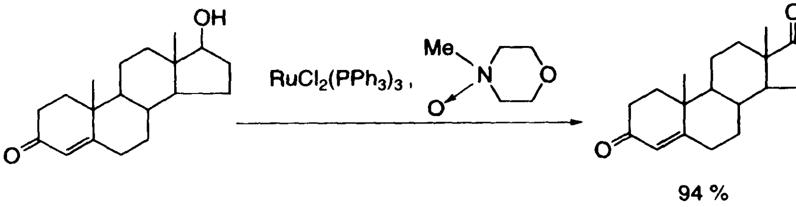
16.5.2 OXIDATIONS

$RuCl_2(PPh_3)_3$ is liable to bond with the OH of alcohol, and it is able to stoichiometrically and selectively oxidize primary alcohols under certain conditions. For example, as shown in eq. (16.24), only primary OH is oxidized to afford the aldehyde in a high yield, but the secondary OH remains unchanged as it is [72].



$$CH_3\overset{\overset{OH}{|}}{C}H(CH_2)_8CH_2OH \xrightarrow[\text{in benzene}]{RuCl_2(PPh_3)_3,\ 25\ °C,\ 2\ h\ ,\ 89\ \%} CH_3\overset{\overset{OH}{|}}{C}H(CH_2)_8CHO \quad (16.24)$$

$RuCl_2(PPh_3)_3$ is able to oxidize alcohols selectively with oxidizing agents such as a peroxide or N-oxide. For example, as shown in eq. (16.25), a steroid is oxidized with $RuCl_2(PPh_3)_3$ and an N-methylmorphorine-N-oxide to afford the diketon [73].



(16.25)

testosterone

$RuH_2(PPh_3)_4$ is used as a dehydrogenation type oxidation catalyst for alcohols and aldehydes [66a,66b]. For example, the esterification of alcohol, lactone formation from diol, N-alkylation of amine with alcohol, and the condensation of aldehyde with alcohol.

The reaction shown in eq. (16.25a) is the esterification of alcohol [66b]. In this reaction, the reaction mechanism is considered as follows; as the ruthenium has a strong affinity to the oxygen of alcohol and aldehyde, ruthenium bonds to the oxygen and the hydrogen bonded with the oxygen at the α-carbon is dehydrogenated at the same time. This mechanism is virtually the same as the mechanism shown in Scheme 16.6 in which the substrate coordinated to the ruthenium and the hydrogen of the substrate is dehydrogenated at the same time.

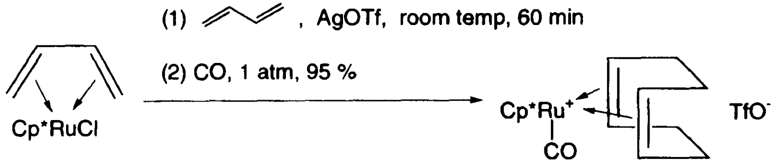
$$C_4H_9OH \xrightarrow[\text{in mesitylene}]{RuH_2(PPh_3)_4,\ 180\ ^\circ C} C_3H_7COOC_4H_9 \qquad (16.25a)$$

Conv. 96 %, Yield 97 %

16.5.3 ADDITION REACTIONS

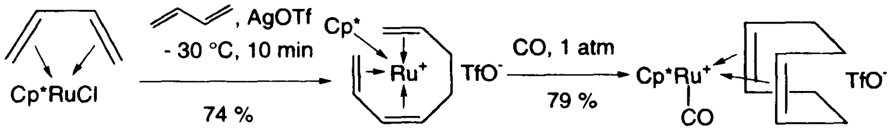
Organoruthenium compounds react with alkenes and alkynes to afford π-complexes as intermediates and addition reaction proceeds [74–79].

(η^5-C_5Me_5)Ru(η^4-butadiene)Cl reacts with butadiene in the presence of trifluoromethanesulfonic acid silver salt, and carbon monoxide reacts to afford 1,5-cyclooctadiene of [4 + 4]cycloaddition product as shown in eq. (16.26) [74]. If the reaction proceeds at low temperatures for a short time, the reaction affords the triene which is formed by the tail-head dimerization of two butadiene as shown in eq. (16.27). The triene is a liable intermediate, it is decomposed in chloroform at 22 °C for 20 hours and it is cyclized under carbon monoxide pressure to afford the carbonyl compounds. The structures of the intermediate triene has been determined by X-ray diffraction studies [74].



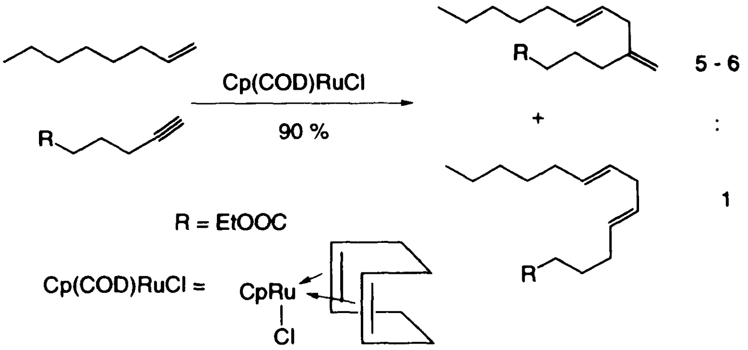
(16.26)

Cp* = η^5-C_5Me_5, AgOTf = silver trifluoromethanesufonate



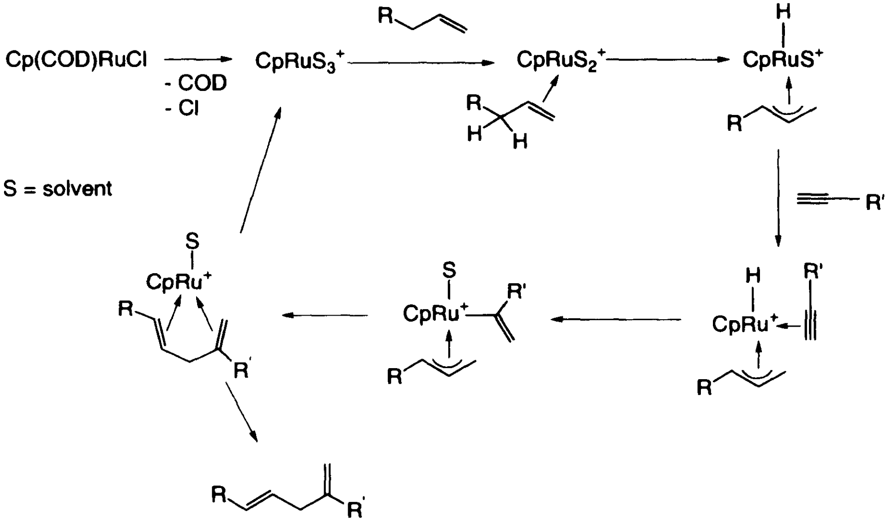
(16.27)

Compounds having carbon–carbon double bond such as alkenes and allylalcohol, add to acetylene compounds in the presence of ruthenium complexes. For example, as shown in eq. (16.28), alkene adds with 1,2-addition to alkyne without influence of the functional group [78]. It is considered that the addition proceeds by the coordination of two unsaturated groups to the ruthenium atom as shown in Scheme 16.6 [75].



(16.28)

Nucleophilic addition of $RuH_2(PPh_3)_4$ to nitrile proceeds under neutral conditions or near neutral conditions [66a]. Nitrile reacts with water in the presence of $RuH_2(PPH_3)_4$ catalysts to afford amide in high yield and nitrile reacts with amine in the presence of water to afford amide in a high yield by an addition condensation as shown in eq. (16.28a). Further, dinitrile reacts with diamine to afford a polymeric polyamide by an addition condensation as shown in eq. (16.28b) [66a,79a].



Scheme 16.6 [75]

$$\mathrm{R^1CN\ +\ HNR^2R^3\ +\ H_2O} \xrightarrow[\text{in 1,2-dimethoxyethane}]{\mathrm{RuH_2(PPh_3)_4},\ 160\ ^\circ\mathrm{C},\ 24\ \mathrm{h}} \mathrm{R^1CONR^2R^3\ +\ NH_3} \qquad (16.28a)$$

$R^1 - R^3$ = Me, i-Pr, Bu, etc., Yield = 70 - 97 %

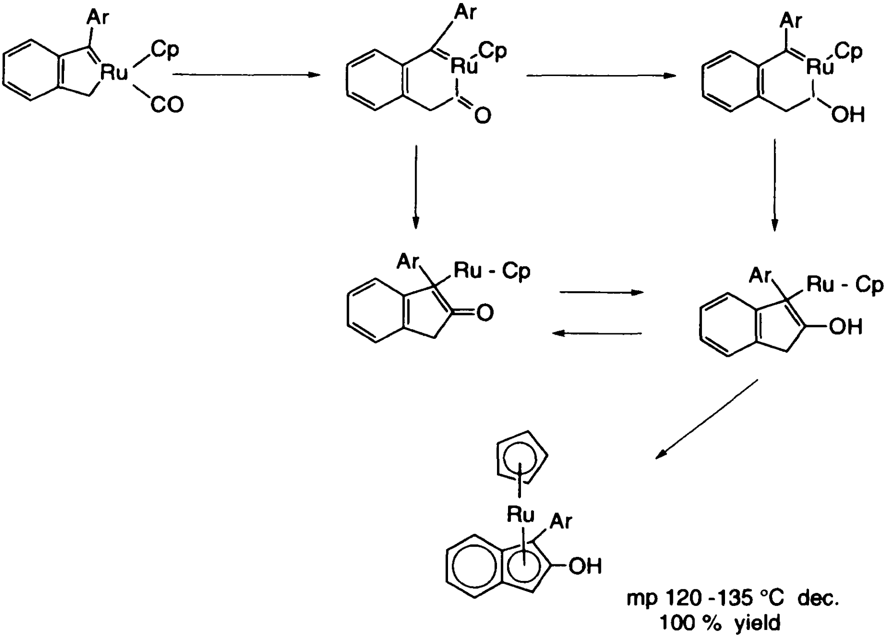
$$\mathrm{NC(CH_2)_4CN\ +\ H_2N(CH_2)_6NH_2\ +\ 2H_2O} \xrightarrow[\text{in 1,2-dimethoxyethane}]{\mathrm{RuH_2(PPh_3)_4},\ 160\ ^\circ\mathrm{C},\ 24\ \mathrm{h}}$$

$$\mathrm{-[NH(CH_2)_6NHCO(CH_2)_4CO]_n-} \qquad (16.28b)$$

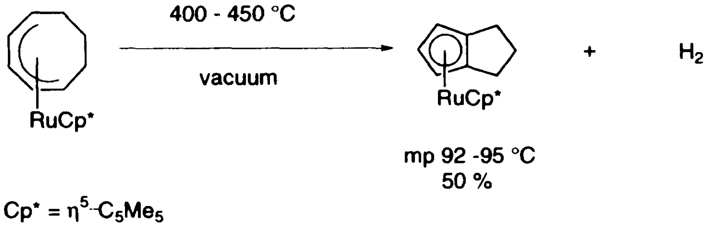
mp 255 °C, MW 8900, Yield 98 %

16.5.4 AROMATIC RING FORMATION REACTIONS

As organoruthenium compounds are able to form the stable ruthenocene, a cyclopentadienyl ring formation reaction tends to proceed. For example, as shown in Scheme 16.7, a metallaindene of ruthenium is heated, and ruthenocene is quantitatively obtained by a carbonyl insertion and a carbene transfer [52]. On the other hand, the gas-phase thermal decomposition of Cp*Ru(η^5-cyclooctadienyl) affords ruthenocene by the formation of cyclopentadienyl ring from a cyclooctadienyl ring as shown in eq. (16.29) [32].

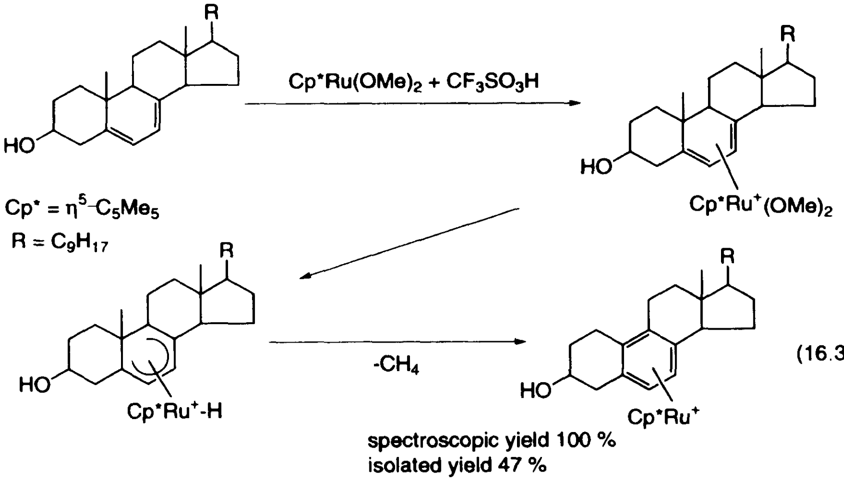


Scheme 16.7 [52]



(16.29)

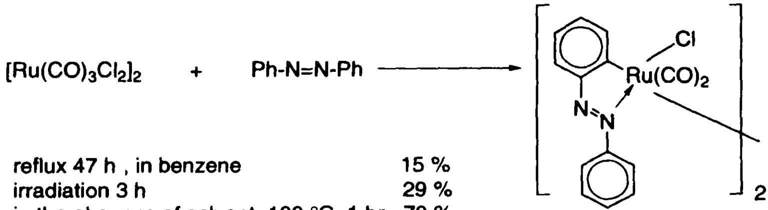
If cyclopentadienylruthenium is changed to Ru^+ by a reaction with CF_3SO_3H, and is liable to bond to a benzene ring of six electrons. As shown in eq. (16.30), the aromatization reaction of 5,7-dienyl steroid with Cp^+Ru compounds and CF_3SO_3H proceeds quantitatively [80].



(16.30)

16.5.5 CYCLOMETALATIONS

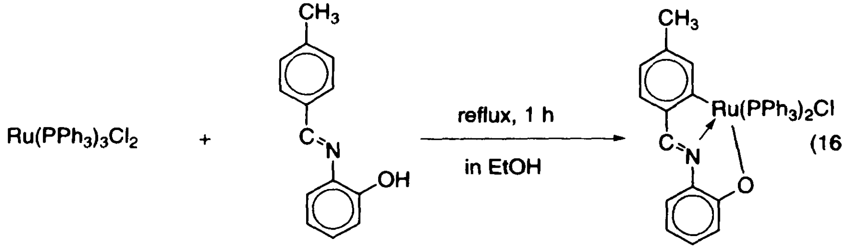
With azobenzene, benzylideneamine, dimethylaminomethylbenzene, etc., cyclometalations proceed to form five-membered ring compounds as shown in eq. (16.31)–(16.34) [81–90c]. Transmetalation is shown in eq. (16.34) [86]. As shown in eq. (16.35), ketimine reacts with ruthenium compounds at room temperatures for a short time to afford the cyclometalation intermediate, further reaction for a long time affords cyclometalation products [87]. The other cyclometalations, e.g., reaction shown in eqs. (16.36) and (16.37), have been reported [88–90].



(16.31)

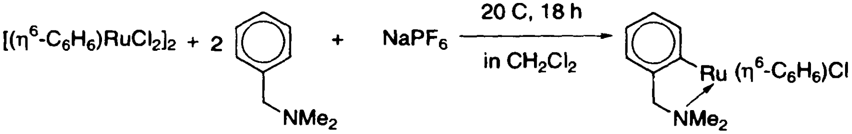
reflux 47 h , in benzene	15 %
irradiation 3 h	29 %
in the absence of solvent, 100 °C, 1 hr	70 %

mp 138 - 140 °C

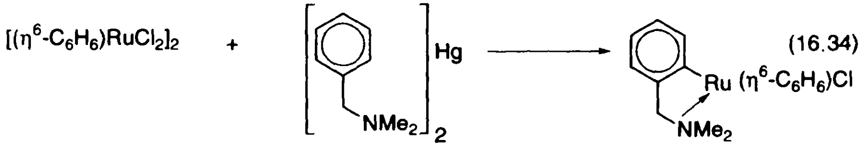


(16.32)

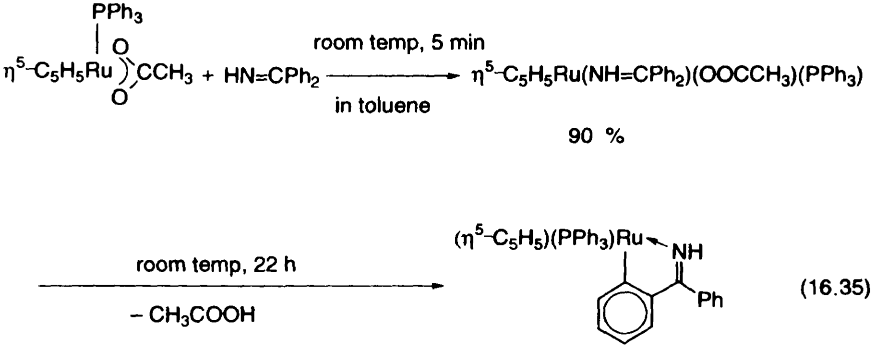
84 %



$+\ C_6H_5CH_2NMe_2{\bullet}PF_6$ (16.33)



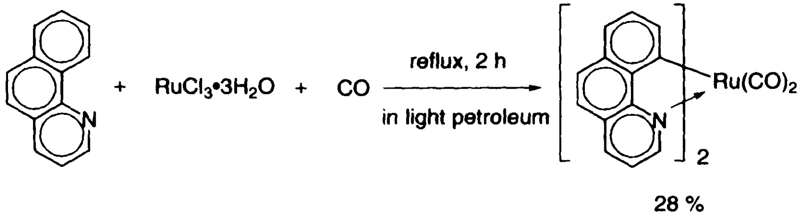
(16.34)



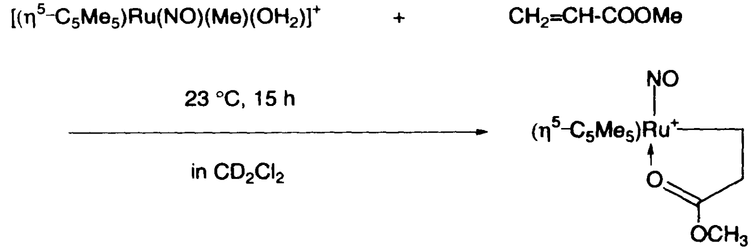
90 %

(16.35)

69 %



(16.36)

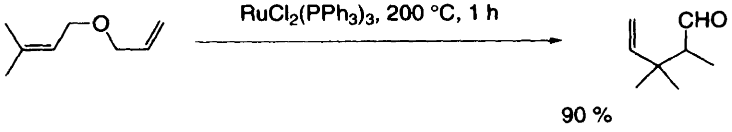


(16.37)

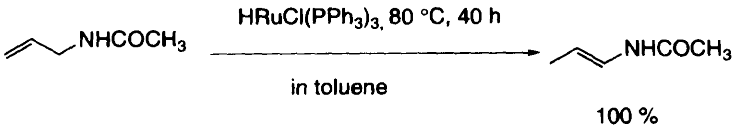
16.5.6 OTHERS

Other reactions with organoruthenium compounds are isomerization, condensation, and reactions with CO or CO_2, etc. [66a,66b].

As ruthenium has a strong affinity to oxygen and nitrogen, the oxygen or nitrogen compounds such as ethers, acetals, ketones, amides and epoxide coordinates to the ruthenium and isomerization proceeds [66a], for example, reactions are shown in eqs. (16.38) and (16.39) [91,92].

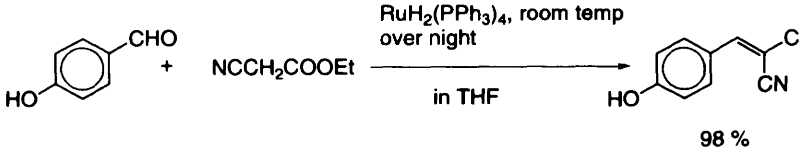


(16.38)

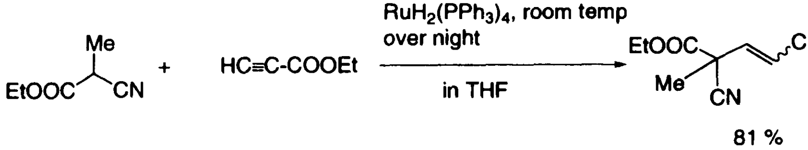


(16.39)

Nitrile reacts with an aldehyde or an electron-withdrawing olefin, an aldol condensation or a Michael addition proceeds under neutral reaction conditions and a carbon–carbon bond forms selectively at the α-position of nitrile [66a,93]. For example, the aldol condensation and Michael addition are shown in eqs. (16.40) and (16.41).



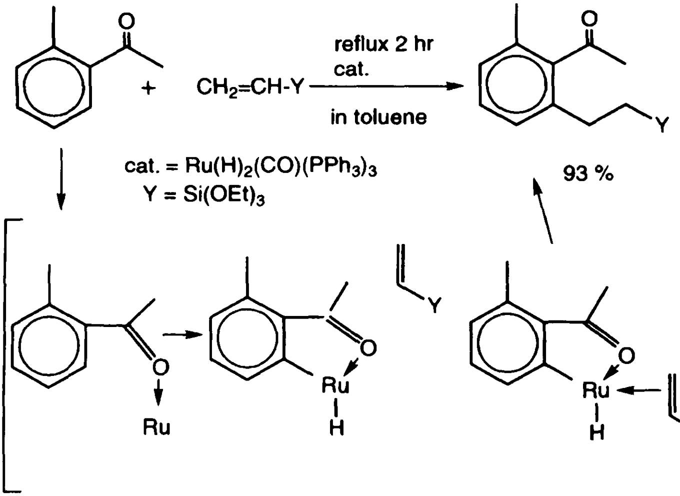
(16.40)



(16.41)

A hydrocarbonation by using synthetic gas, the reaction of carbon monoxide such as a water–gas-shift reaction, a reaction by using carbon dioxide, etc., have been studied with ruthenium catalysts [66a].

Recently, Murai and co-workers have reported a C-H/olefin coupling reaction by utilizing two properties of ruthenium in which the ruthenium tends to form a π-complex with carbon–carbon unsaturated compounds and cyclometalations (orthometalation) are liable to proceed. The representative reaction is shown in eq. (16.42) [94–96]. $RuH_2(CO)(PPh_3)_3$ and $Ru(CO)_2(PPh_3)_3$ are used as the catalysts.



(16.42)

At first it was thought that orthometalation to methylphenylketone proceeds, and the ruthenium compound forms the π-complex with a carbon–carbon unsaturated bond, and then the carbon–carbon double bond is substituted with ruthenium, and that a selective substitution reaction proceeds at the 2-position.

REFERENCES

[1] *Kagaku Daijiten*, Tokyo Kagaku Doojin, Tokyo, p. 2528, 1989.

[2] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.

[3] T. Muroi, *Shokubai*, **36** (1994) 531.

[4] *Sekai Dai Hyakkajiten*, Heibonsha, Tokyo, Vol. 30, p. 34, 1988.

[5] *Sekai Kagaku Daijiten, Technopia (Encyclopedia of Science and Technology)*, Kodansha, Tokyo, Vol. 18, p. 294, 1977.

[6] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., John Wiley, New York, vol. 18, p. 228, 1980.

[7] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, 4th ed., p. 1388, 1987.

[8] *Jikken Kagaku Kouza 18, 4th ed.*, "Yuki Kinzoku Sakutai", Japan Chem. Soc. ed., Maruzen, Tokyo, p. 254, 1991.

[9] M.I. Bruce, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 4, p. 651, 1982.

[10] F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, **6** (1967) 1220.

[11] J.R. Moss and W.A.G. Graham, *J. Chem. Soc. Dalton Trans.*, (1977) 95.

[12] M.I. Bruce and F.G.A. Stone, *J. Chem. Soc. A*, (1967) 1238.

[13] M.J. Cleare and W.P. Griffith, *J. Chem. Soc. A*, (1969) 372.

[14] N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, *Inorg. Synth.*, **15** (1974) 45.

[15] P. Pertici, G. Vitulli and L. Porri, *J. Chem. Soc. Commun.*, (1975) 846.

[16] P. Pertici, G. Vitulli, M. Paci and L. Porri, *J. Chem. Soc. Dalton Trans.*, (1980) 1961.

[17] M.A. Bennet, M.I. Bruce and T.W. Matheson, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 4, p. 691, 1982.

[18] K. Itoh, H. Nagashima, T. Ohshima, N. Ohshima and H. Nishiyama, *J. Organomet. Chem.*, **272** (1984) 179.

[19] M.A. Bennett and A.K. Smith, *J. Chem. Soc. Dalton Trans.*, (1974) 233.

[20] H.L. Bozec, D. Touchard and P.H. Dixneuf, *Adv. Organomet. Chem.*, **29** (1989) 163.

[21] S.G. Davies, J.P. Mcnally and A.J. Smallridge, *Adv. Organomet. Chem.*, **30** (1990) 1.

[22] R.D. Wilson, S.M. Wu, R.A. Love and R. Bau, *Inorg. Chem.*, **17** (1978) 1271.

[23] A.J. Deeming, S.S. Ullah, A.J.P. Domingos, B.F.G. Johnson and J. Lewis, *J. Chem. Soc. Dalton Trans.*, (1974) 2093.

[24] A.P. Humphries and S.A.R. Knox, *J. Chem. Soc. Dalton Trans.*, (1975) 1710.

[25] J.W. Benson and R.J. Angelichi, *Inorg. Chem.*, **32** (1993) 1871.

[26] R.S. Hay-Motherwell, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1992) 3477.

[27] B.K. Campion, R.H. Heyn, T.D. Tilley and A.L. Rheingold, *J. Am. Chem. Soc.*, **115** (1993) 5527.

[28] J.F. Hartwing, R.G. Bergman and R.A. Andersen, *J. Am. Chem. Soc.*, **113** (1991) 3404.

[29] S.D. Robinson and M.F. Uttley, *J. Chem. Soc. Dalton Trans.*, (1973) 1912.

[30] G.L. Hardgrove and D.H. Templeton, *Acta Cryst.*, **12** (1959) 28.

[31] C.H. Winter, Y.-H. Han, R.L. Ostrander and A.L. Rheingold, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 1161.

[32] R.U. Kirss, A. Quazi, C.H. Lake and M.R. Chuchill, *Organometallics*, **12** (1993) 4145.

[32a] J.M. Nelson, A.J. Lough and I. Manners, *Organometallics*, **13** (1994) 3703.

[32b] T. Hayashi, A. Ohno, S. Lu, Y. Matsumoto, E. Fukuyo and K. Yanagi, *J. Am. Chem. Soc.*, **116** (1994) 4221.

[33] F. Kvietok, V. Allured, V. Carperos and M.R. DuBois, *Organometallics*, **13** (1994) 60.

[34] S. Suravajjala, J.R. Polam and L.C. Porter, *J. Organomet. Chem.*, **461** (1993) 201.

[35] S. Suravajjala, J.R. Polam and L.C. Porter, *Organometallics*, **13** (1994) 37.

[36] D.T. Glatzhofer, Y. Liang, G.P. Funkhouser and M.A. Khan, *Organometallics*, **13** (1994) 315.

[37] S.A. Lomenzo, S.P. Nolan and M.L. Trudell, *Organometallics*, **13** (1994) 676.

[38] J.W. Steed and D.A. Tocher, *J. Chem. Soc. Dalton Trans.*, (1993) 3187.

[39] G.E. Herberich, U. Englert and F. Marken, *Organometallics*, **12** (1993) 4039.

[40] G.E. Herberich, U. Englert, D. Pubanz and P. Hofmann, *J. Organomet. Chem.*, **459** (1993) 1.

[41] J.R. Pipal and R.N. Grimes, *Organometallics*, **12** (1993) 4452.

[42] M.I. Bruce, F.S. Wong, B.W. Skelton and A.H. White, *J. Chem. Soc. Dalton Trans.*, (1981) 1398.

[43] K.-T. Smith, C. Rømming and M. Tilset, *J. Am. Chem. Soc.*, **115** (1993) 8681.

[44] J.R. Lomprey and J.P. Selegue, *Organometallics*, **12** (1993) 616.

[45] J.R. Lomprey and J.P. Selegue, *J. Am. Chem. Soc.*, **114** (1992) 5518.

[46] F.R. Lemke, D.J. Szalda and R.M. Bullock, *J. Am. Chem. Soc.*, **113** (1991) 8466.

[47] J.L. Hubbard, A. Morneau, R.M. Burns and O.W. Nadeau, *J. Am. Chem. Soc.*, **113** (1991) 9180.

[48] A. Shaver and P.-Y. Plouffe, *J. Am. Chem. Soc.*, **113** (1991) 7780.

[49] M.H. Wang, U. Englert and U. Kölle, *J. Organomet. Chem.*, **453** (1993) 127.

[50] W. Lunginbühl, P. Zbinden, P.A. Pittet, T. Armbruster, H.-B. Bürgi, A.E. Merbach and A. Ludi, *Inorg. Chem.*, **30** (1991) 2350.

[51] F.B. McCormick, D.D. Cox and W.B. Gleason, *Organometallics*, **12** (1993) 610.

[52] J. Yang, J. Yin, K.A. Abboud and W.M. Jones, *Organometallics*, **13** (1994) 971.

[53] P. Barabotti, P. Diversi, G. Ingrosso, A. Luncherini, F. Marchetti, L. Sagramora, V. Adovasio and M. Nardelli, *J. Chem. Soc. Dalton Trans.*, (1990) 179.

[54] J.B. Hoke, L.S. Hollis and E.W. Stern, *J. Organomet. Chem.*, **455** (1993) 193.

[55] Z. Lin and M.B. Hall, *Organometallics*, **12** (1993) 19.

[56] J. Müller, K. Oiao, M. Siewing and B. Westphal, *J. Organomet. Chem.*, **458** (1993) 219.

[57] S. Luo, T.B. Rauchfuss and S.R. Wilson, *J. Am. Chem. Soc.*, **114** (1992) 8515.

[58] P. Pertici, E. Pitzalis, F. Marchetti, C. Rosini, P. Salvadori and M.A. Bennett, *J. Organomet. Chem.*, **466** (1994) 221.

[59] C.E.F. Rickard, W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, *J. Organomet. Chem.*, **389** (1990) 375.

[59a] A.C. Skapski and P.G.H. Troughton, *J. Chem. Soc. Commun.*, (1968) 1230.

[59b] S.J.L. Placa and J.A. Ibers, *Inorg. Chem.*, **4** (1965) 778.

[60] R.E. Cobbledick, F.W.B. Einstein, R.K. Pomeroy and E.R. Spetch, *J. Organomet. Chem.*, **195** (1980) 77.

[61] Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh and J.Y. Satoh, *J. Am. Chem. Soc.*, **113** (1991) 9604.

[62] G.R. Clark, K.R. Flower, W.R. Roper and L.J. Wright, *Organometallics*, **12** (1993) 3810.

[63] S. Merlino and G. Montagnoli, *Acta Cryst.*, **B24** (1968) 424.

[64] J.D. Gargulak, M.D. Noirot and W.L. Gladfelter, *J. Am. Chem. Soc.*, **113** (1991) 1054.

[64a] Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh and J.Y. Satoh, *J. Am. Chem. Soc.*, **113** (1991) 9604.

[64b] Y. Wakatsuki, N. Koga, H. Yamazaki and K. Morokuma, *J. Am. Chem. Soc.*, **116** (1994) 8105.

[64c] Z. Wu, S.T. Nguyen, R.H. Grubbs and J.W. Ziller, *J. Am. Chem. Soc.*, **117** (1995) 5503.

[65] M.R. Churchill, F.J. Hollander and J.P. Hutchinson, *Inorg. Chem.*, **16** (1977) 2655.

[66] R. Mason and A.I.M. Rae, *J. Chem. Soc. A*, (1968) 778.

[66a] S. Murahashi and T. Naota, *Yuki Gosei Kagaku Kyokaishi*, **46** (1988) 930.

[66b] S. Murahashi and T. Naota, *Sekiyu Gakkaishi*, **34** (1991) 1.

[67] A. Yamamoto ed., *Yuki Kinzoku Kagaku Kagoubutsu, Goseihou oyobi Riyouho*, Tokyo Kagaku Dojin, Tokyo, p. 164, 1991.

[68] *Jikken Kagaku Kouza 25, 4th ed., Yuki Gosei VII*, Japan Chemical Society ed., Maruzen, Tokyo, p. 440, 1991.

[69] Y. Watanabe, T. Ohta, Y. Tsuji, T. Hiyoshi and Y. Tsuji, *Bull. Chem. Soc. Japan*, **57** (1984) 2440.

[70] H. Takaya, T. Ohta, N. Sayo, H. Kumobayashi, S. Akutagawa, S. Inoue, I. Kasahara and R. Noyori, *J. Am. Chem. Soc.*, **109** (1987) 1596.

[71] W.-C. Chan, C.-P. Lau, L. Cheng and Y.-S. Leung, *J. Organomet. Chem.*, **464** (1994) 103.

[72] H. Tomioka, K. Takai, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, (1981) 1605.

[73] K.B. Sharpless, K. Akashi and K. Oshima, *Tetrahedron Lett.*, (1976) 2503.

[74] K. Itoh, K. Masuda, T. Fukahori, K. Nakano, K. Aoki and H. Nagashima, *Organometallics*, **13** (1994) 1020.

[75] M. Trost and A. Indolese, *J. Am. Chem. Soc.*, **115** (1993) 4361.

[76] B.M. Trost, J.A. Martinez, R.J. Kulawiec and A.F. Indolese, *J. Am. Chem. Soc.*, **115** (1993) 10402.

[77] B.M. Trost, K. Imi and A.F. Indolese, *J. Am. Chem. Soc.*, **115** (1993) 8831.

[78] T. Mitsudo, Y. Hori and Y. Watanabe, *Bull. Chem. Soc. Japan* (1986) 3201.

[79] T. Mitsudo, Y. Nakagawa, K. Watanabe, Y. Hori, H. Misawa, H. Watanabe and Y. Watanabe, *J. Org. Chem.*, **50** (1985) 565.

[79a] S. Murahashi, T. Naota and E. Saito, *J. Am. Chem. Soc.*, **108** (1986) 7846.

[80] M.A. Halcrow, F. Urbanos and B. Chaudret, *Organometallics*, **12** (1993) 955.

[81] M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, *J. Chem. Soc. A*, (1971) 2820.

[82] M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, *J. Chem. Soc. Commun.*, (1970) 1325.

[83] J.D. Gilbert, D. Rose and G. Wilkinson, *J. Chem. Soc. A*, (1970) 2765.

[84] M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, *J. Chem. Soc. A*, (1970) 3204.

[85] P. Ghoshi, A. Pramanik, N. Bag, G.K. Lahiri and A. Chakravorty, *J. Organomet. Chem.*, **454** (1993) 237.

[86] H.C.L. Abbenhuis, M. Pfeffer, J.-P. Sutter, A. de Cian, J. Fischer, H.L. Ji and J.H. Nelson, *Organometallics*, **12** (1993) 4464.

[87] H. Werner, T. Daniel, W. Knaup and O. Nürnberg, *J. Organomet. Chem.*, **462** (1993) 309.

[88] M.I. Bruce, B.L. Goodall and F.G.A. Stone, *J. Organomet. Chem.*, **60** (1973) 343.

[89] E. Hauptman, M. Brookhart, P.J. Fagan and J.C. Calabrese, *Organometallics*, **13** (1994) 774.

[90] I. Omae, *Organometallic Intramolecular-coordination Compounds, J. Organometallic Chemistry Library 18*, Elsevier, Amsterdam, 1986.

[90a] G.K. Lahiri, S. Bhattacharya, M. Mukherjee, A.K. Mukherjee and A. Chakravorty, *Inorg. Chem.*, **26** (1987) 3359.

[90b] D.E. Linn, Jr. and J. Halpern, *J. Organomet. Chem.*, **330** (1987) 155.

[90c] V. Massonneau, P.L. Maux and G. Simonneaux, *J. Organomet. Chem.*, **327** (1987) 269.

[91] J.M. Reuter and R.G. Salomon, *J. Org. Chem.*, **42** (1977) 3360.

[92] J.K. Stille and Y. Becker, *J. Org. Chem.*, **45** (1980) 2139.

[93] T. Naota, H. Taki, M. Mizuno and S. Murahashi, *J. Am. Chem. Soc.*, **111** (1989) 5954.

[94] S. Murai, N. Chatani and F. Kakiuchi, *Shokubai*, **36** (1994) 565.

[95] F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani and S. Murai, *Bull. Chem. Soc. Japan*, **68** (1995) 62.

[96] F. Kakiuchi, Y. Yamamoto, N. Chatani and S. Murai, *Chem. Lett.*, (1995) 681.

17 Organocobalt Compounds

17.1 INTRODUCTION

Cobalt is an element known from cobalt blue, cobalt irradiation, metals in special steels and magnetic materials, etc. Cobalt is one element of vitamin B_{12} which is one of the indispensable human nutrients. Generally, cobalt is widely studied in the chemistry of complexes since it is liable to form complex salts. But organocobalt compounds are not known unlike the complex salts. However, recently their organosynthetic uses have been rapidly increasing.

17.2 COBALT

Cobalt belongs to group 9 of the periodic table. The outer electronic configuration is $3d^7 4s^2$, and Rh and Ir are elements of the same group. Cobalt exists at 20 ppm similar to Pb (14 ppm), Li (20 ppm) and Cu (50 ppm) in the Earth's crust [1]. The ores of cobalt are sulfide, oxide and arsenide ores [2–8]. Sulfide and oxide ores contain 2–2.5% of cobalt. These ores dissolves in sulfuric acid directly or after sulfatizing by roasting the ores, and the copper is separated by an electrolysis. Iron and aluminum are removed from the residual fluid of electrolysis by regulating the pH. Further nickel and zinc are removed as their sulfates by adding NaHS, H_2S, Na_2CO_3, etc. and cobalt hydrate ($Co(OH)_2$) is precipitated by adding lime. 99.90% pure cobalt is prepared by electrolysis of $Co(OH)_2$ [3,4].

Cobalt is similar to silver in appearance, is stable and forms a scale only on the surface during exposure to air. It dissolves gradually in acids to evolve hydrogen and it easily dissolves in an oxidizing acid to form a cobalt(II) salt. It is passivated by strong oxidizing agents such as dichromates and nitric acid. Cobalt combines readily with sulfur, phosphorus, arsenic, halogen and silicon by heating, but it does not react with hydrogen or nitrogen [5,6,8]. The properties of cobalt is shown in Table 17.1.

Cobalt is a close-packed hexagonal α type below 417 °C and transforms to a face-centered cubic β type above 417 °C [2,3].

Cobalt is used for magnetic materials, heat-resistant alloys, cutting-tool material, hydrogenation catalysts, etc. Cobalt chloride, cobalt sulfate and cobalt carbonate are used for pigments in the glass and ceramic industries, and driers for inks and paints. The half-life of the radioactive isotope ^{60}Co is 5.6 y and it emits γ-rays by β-disintegration. These γ-rays are used for the treatment of tumors.

Table 17.1 Properties of cobalt [2,3]

Property	Value
melting point, °C	1493
boiling point, °C	3100
crystal structure	close-packed hexagonal
density, 20 °C, g/cm^3	8.80
specific heat at 25 °C, J g^{-1}	0.442
latent heat of fusion, J g^{-1} K^{-1}	259.4
latent heat of vaporization, J g^{-1}	6276
transformation temperature, °C	417
heat of transformation, J/mol	251
hardness, Mors scale	5.6
Vickers (purity 99.98%) at 20 °C	253
coefficient of thermal expansion,	
at room temperature, K^{-1}	12.5
resistivity at 20 °C, 10^{-8} Ω m	6.24
thermal conductivity,	
at room temperature, W m^{-1} K^{-1}	69.16
Curie temperature, °C	1121

17.3 PREPARATIONS OF ORGANOCOBALT COMPOUNDS

Organocobalt compounds are prepared by the following six reaction methods, similar to those for organomanganese compounds (Chapter 14) [9].

(1) Reductive carbonylations
(2) Reactions with cobaltcarbonyls
(3) Reactions with organoalkali metal compounds
(4) Reactions with organomagnesium compounds
(5) Metal vapor synthesis
(6) Others

7.3.1 REDUCTIVE CARBONYLATIONS

The basic compound for the synthesis of organocobalt compounds is $Co_2(CO)_8$ which satisfies the 18-electron rule [10–17]. $Co_2(CO)_8$ is prepared by reducing cobalt acetate, cobalt hydroxide or cobalt oxalate with hydrogen and reacting with carbon monoxide [10–13]. For example, $Co_2(CO)_8$ is prepared by reacting cobalt acetate with hydrogen and carbon monoxide as shown in eq. (17.1) [11]. The reaction is carried out under mild conditions by adding a small amount of $Co_2(CO)_8$ since $Co_2(CO)_8$ has an autocatalytic action as shown in eq. (17.2) [12].

The reactive cobalt metal, which is obtained by reducing a compound with hydrogen, is able to react directly with carbon monoxide to afford $Co_2(CO)_8$ almost quantitatively as shown in eq. (17.3) [10].

$Co_2(CO)_8$ is an orange crystal (mp 51 °C), it ignites in air, and dissolves in organic solvents. As $Co_2(CO)_8$ releases carbon monoxide at room temperature to yield $Co_4(CO)_{12}$, it should be stored at 0 °C or below under an inert gas or carbon monoxide atmosphere [10].

$$2Co(OAc)_2{\bullet}4H_2O + 8(CH_3CO)_2O + 8CO + 2H_2 \xrightarrow[\text{in acetic acid}]{\substack{160-180\ ^\circ C,\ 2\ h \\ 200\ atm}} \underset{60\%}{Co_2(CO)_8} + 20CH_3COOH \quad (17.1)$$

$$2Co(OH)_2 + 8CO + 2H_2 \xrightarrow[\text{in PrOH}]{\substack{55-60\ ^\circ C,\ 6\ hr \\ 50\ atm,\ Co_2(CO)_8}} \underset{33\%}{Co_2(CO)_8} + 4H_2O \quad (17.2)$$

$$Co + CO \xrightarrow{150-170\ ^\circ C,\ 200\ atm} \underset{99\%}{Co_2(CO)_8} \quad (17.3)$$

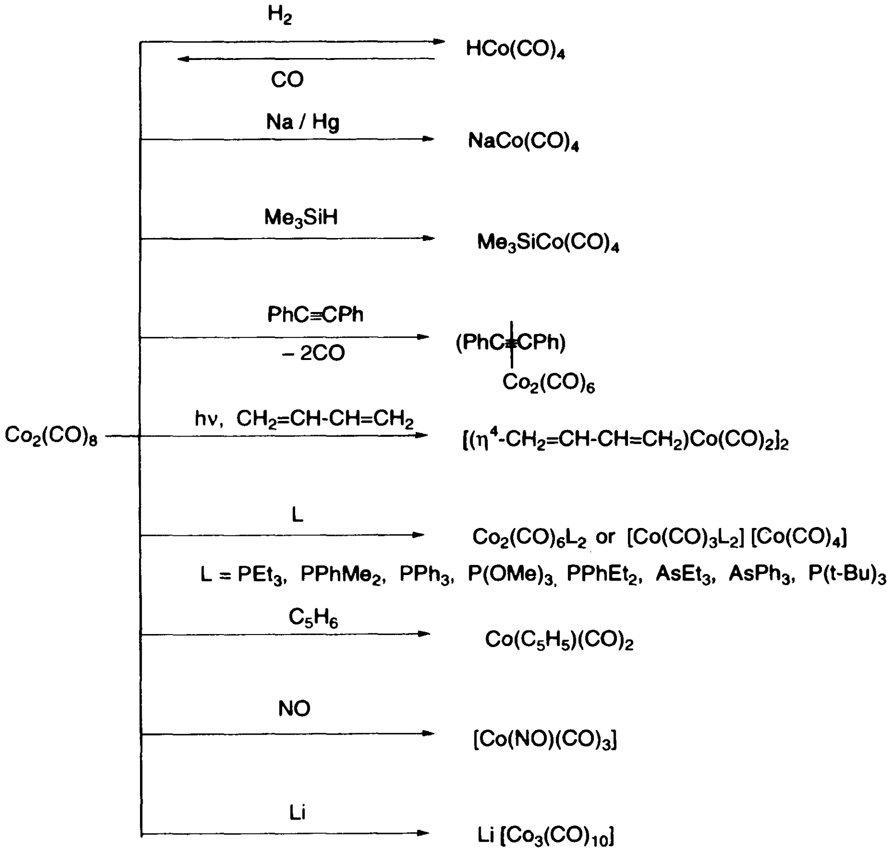
17.3.2 REACTIONS WITH COBALTCARBONYLS

$Co_2(CO)_8$, the basic compound of organocobalt compounds, reacts with many compounds to afford the variety of organocobalt compounds as shown in Scheme 17.1. In these products, $NaCo(CO)_4$ [12] or $HCo(CO)_4$ [16], obtained by reaction with sodium or hydrogen, are also used as the raw materials for the synthesis of organocobalt compounds.

$HCo(CO)_4$ is also prepared in high yield by the reaction of $Co_2(CO)_8$ with pyridine and sulfuric acid as shown in eq. (17.4) [12,13]. With $NaCo(CO)_4$ and $HCo(CO)_4$ as raw materials, organocobalt compounds are prepared as shown in eqs. (17.5) and (17.6) [12].

$$3Co_2(CO)_8 + 12C_5H_5N \longrightarrow 2[Co(C_5H_5N)_6][Co(CO)_4]_2 + 8CO$$

$$2[Co(C_5H_5N)_6][Co(CO)_4]_2 + 8H_2SO_4 \longrightarrow \underset{80-90\%}{4HCo(CO)_4} + 2CoSO_4 + 6(C_5H_5NH)_2SO_4 \quad (17.4)$$



Scheme 17.1 [10,12].

$$\mathrm{NaCo(CO)_4 + CH_2{=}CH{-}CH_2Br \xrightarrow[\text{in } Me_2O]{0\ ^\circ C,\ \text{over night}} \underset{66\%}{(\eta^3\text{-}C_3H_5)Co(CO)_3} + NaBr + CO} \qquad (17.5)$$

$$\mathrm{HCo(CO)_4 + CH_2{=}C(CH_3)_2 \longrightarrow (CH_3)_3CCo(CO)_4} \qquad (17.6)$$

17.3.3 REACTIONS WITH ALKALI METAL COMPOUNDS

Organocobalt compounds are prepared by the reaction of organoalkali metal compounds with cobalt halides. For example, sodium cyclopentadiene reacts with cobalt chloride in THF, the solvent is evaporated, and the dark purple crystals of cobaltocene are obtained by sublimating at 60–200 °C under a high vacuum as shown in eq. (17.7) [12].

$$\mathrm{CoCl_2} + \mathrm{2NaC_5H_5} \xrightarrow[\text{in THF}]{\text{reflux, 2 hr}} \underset{\substack{\text{mp 173 - 174°C} \\ 90\%}}{\mathrm{Co(C_5H_5)_2}} + \mathrm{2NaCl} \qquad (17.7)$$

Organocobalt compounds are also prepared in high yield by the reaction of a cobalt alkali metal compound with organic halides as shown in eq. (17.8) [17].

$$\mathrm{EtOOCCH_2Br} + \mathrm{NaCo(CO)_4} \xrightarrow[\text{in THF}]{\text{0° C, 50 min}} \underset{\text{practically quantitative yield}}{\mathrm{EtOOCCH_2Co(CO)_4}} + \mathrm{NaBr} \qquad (17.8)$$

17.3.4 REACTIONS WITH ORGANOMAGNESIUM COMPOUNDS

Cobalt halides react with organomagnesium compounds, such as Grignard reagents, like organoalkali metal compounds to afford organocobalt compounds as shown in eq. (17.9) [12].

$$\mathrm{CoBr_2} + \mathrm{2C_6F_5MgBr} \xrightarrow[\text{in THF}]{\text{reflux, 2 h}} \mathrm{Co(C_6F_5)_2} \xrightarrow[\text{in hexane}]{\text{CO, 8 h}} \underset{82\%}{\mathrm{C_6F_5Co(CO)_4}} \qquad (17.9)$$

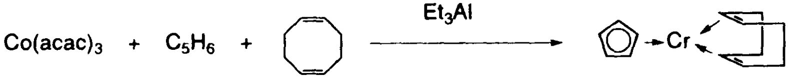
17.3.5 METAL VAPOR SYNTHESIS

Cobalt is able to react directly with organic halides by evaporating to afford organocobalt compounds. For example, as shown in eq. (17.10), cobalt metal is heated by a tungsten wire coated with aluminum oxide, is evaporated under 10^{-5} Torr, and reacts with the solution of bromotetrafluorobenzene and toluene under cooling by liquid nitrogen to afford $(\eta^6\text{-}C_6H_5Me)Co(C_6F_5)_2$ [17].

$$\mathrm{2Co} + \mathrm{2C_6F_5Br} + \mathrm{C_6H_5Me} \xrightarrow{\substack{\text{(i) -196 °C, } 10^{-5} \text{ Torr} \\ \text{(ii) ambient temp.}}} \underset{\substack{\text{red brown} \\ 8 - 20\%}}{(\eta^6\text{-}\mathrm{C_6H_5Me})\mathrm{Co(C_6F_5)_2}} + \mathrm{CoBr_2} \qquad (17.10)$$

17.3.6 OTHERS

As the outer electron configuration of cobalt is $3d^74s^2$ as described above, cobalt is liable to bond with nine electrons to satisfy the 18-electron rule. Hence, cobalt bonded with five electrons from a cyclopentadienyl ring is liable to bond with four electrons such as those from butadiene, cyclooctadiene and a variety of other diene compounds. For example, cobalt acetylactonate reacts with cyclopentadiene and cyclooctadiene in the presence of an organoaluminum compound as a reducing agent to give the cobalt compound coordinated by a five-electron cyclopentadienyl ring and four-electron cyclooctadiene as shown in eq. (17.11) [12].



(17.11)

Cobalt compounds are able to react with nitrogen gas to afford a dinitrogen complex. For example, as shown in eqs. (17.12) and (17.13), cobalt compounds and phosphine react with nitrogen in the presence of a reducing agent such as R_3Al (eq. 17.12) or after reduction with $NaBH_4$ (eq. 17.13) to afford the dinitrogen complex [13,13d].

$$\mathrm{Co(acac)_3 + 3PPh_3 + N_2 \xrightarrow{R_3Al} CoH(N_2)(PPh_3)_3} \qquad (17.12)$$

$$\mathrm{CoCl_2{\bullet}6H_2O + 3PPh_3 \xrightarrow{NaBH_4} CoH_3(PPh_3)_3 \xrightarrow{N_2} CoH(N_2)(PPh_3)_3} \qquad (17.13)$$

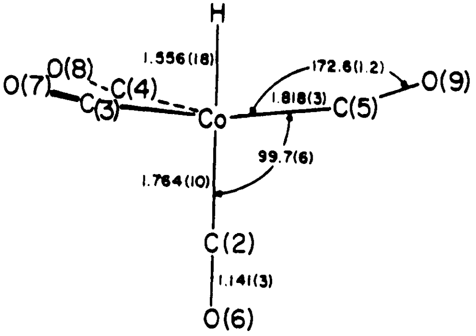
17.4 STRUCTURES OF ORGANOCOBALT COMPOUNDS

$HCo(CO)_4$ is an 18-electron compound coordinated with eight electrons of carbonyl group and one electron of hydrogen. It forms the trigonal bipyramidal structure of five coordination as shown in Figure 17.1. The hydrogen is located in the axial position, the equatorial carbonyl groups bend slightly toward the hydrogen ligand and away from the axial carbonyl [[18].

The most stable structure of $Co_2(CO)_8$ [19–23] is a square pyramidal structure as shown in Figure 17.2. Six carbonyl groups are in symmetry and two carbonyls form a bridged structure [19]. $Mn_2(CO)_{10}$ forms staggered structures as described in Chapter 14, but the staggered structure of $Co_2(CO)_8$ is in a higher energy by 22.3 kcal/mol than that of the square pyramid as shown in Figure 17.2 [19,21].

As π-allyl compounds donate three electrons, $(\eta^3\text{-}C_3H_5)Co(CO)_2(PPh_3)$ is also an 18-electron compound with the four electrons of carbonyl and the two electrons of phosphine. The cobalt atom forms a distorted square pyramidal structure with a formally bidentate η^3-allyl ligand, a phosphine and one carbonyl in the basal positions as shown in Figure 17.3 [24].

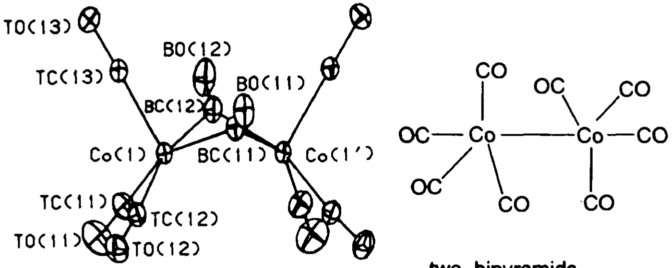
Cyclopentadienyl compound coordinated with five electrons is liable to bond a four-electron donor ligand such as a cycloolefin and a diene as shown in eq. (17.11) [10,25–27]. In Figure 17.4, for example, cyclopentadienyl cobalt phosphine metallocyclopentadiene is shown in Figure 17.4 [28].



Co - H = 1.56 Å

trigonal bipyramidal structure

Figure 17.1 Molecular structure of $HCo(CO)_4$ [18].



two bipyramids
staggered conformation

Figure 17.2 Molecular structure of $Co_2(CO)_8$ [19,21].

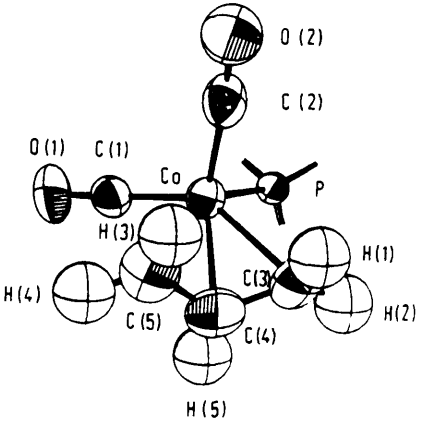
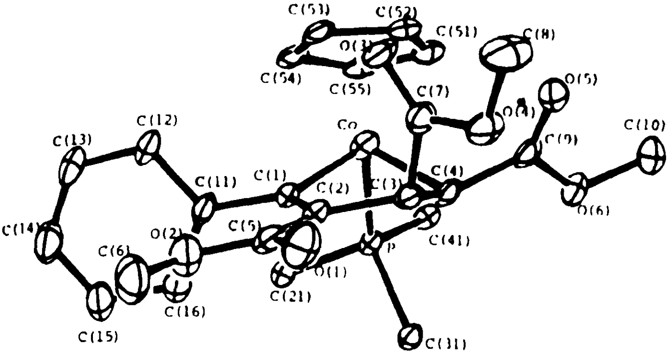


Figure 17.3 Structure of $(\eta^3\text{-}C_3H_3)Co(CO)_2PPh_3$ [24].



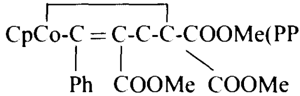
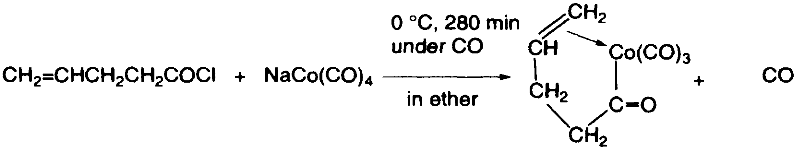


Figure 17.4 Molecular geometry of $\mathrm{CpCo\text{-}\underset{Ph}{C}{=}\underset{COOMe}{C}\text{-}C\text{-}\underset{COOMe}{C}\text{-}COOMe(PPh_3)}$ [28].

Cobaltocene forms a staggered structure (the same as ferrocene), but the cobaltocene is not as stable as ferrocene since it is a 19-electron compound [19–31]. As multiple-deckered cobalt compounds, triple-decker, tetra-decker and hexa-decker compounds are synthesized and their structures have been determined by X-ray diffraction studies [32–33a].

As a cobalt atom tends to bond with a carbon–carbon double bond, it is able to form a 5.5-membered ring compound by an intramolecular coordination bond as shown in eq. (17.14) [34,35].



(17.14)

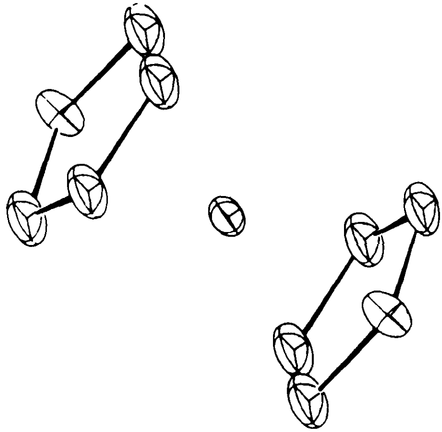
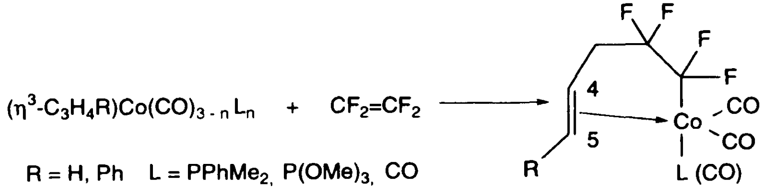


Figure 17.5 Molecular structure of Cp_2Co [29].

Further, the 5.5-membered ring is formed by the insertion of an olefin to a η^3-allyl cobalt compound. The structure of the phosphine derivative is determined by X-ray diffraction studies [36].

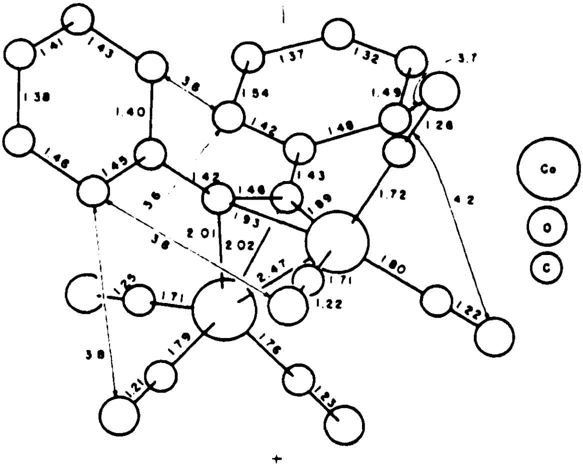


(17.15)

R = H, L = P(OMe)$_3$: Co - C^4 = 2.110 Å
Co - C^5 = 2.116 Å

The structure of dicobalt hexacarbonyl diphenylacetylene is shown in Figure 17.6. Two π-orbitals of the carbon–carbon triple bond bond to two cobalt atoms. The bond length of C–C is slightly longer (1.46 Å) than that of an ordinary carbon–carbon double bond. The cobalt atom forms a distorted octahedral configuration [37].

Many intramolecular coordination compounds with olefins or the orthometalation compounds of organocobalt compounds have also been reported [10,37a–39a].



C - C = 1.46 Å
Co - C - Co = 77°, 78°

Figure 17.6 Molecular structure of (PhC≡CPh)$Co_2(CO)_6$ [37].

17.5 REACTION OF ORGANOCOBALT COMPOUNDS

In the organocobalt compounds, the following seven reactions proceed:

(1) Cyclization reaction of acetylenes and olefins
(2) Cyclization of diacetylenes
(3) Pauson–Khand reactions
(4) Nicolas reaction
(5) Reactions with organocobalt compounds as protecting group
(6) Carbonylations
(7) others

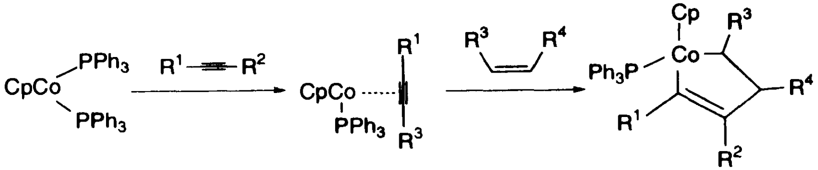
17.5.1 CYCLIZATION OF ACETYLENES AND OLEFINS

Cyclopentadienylcobalt compounds cyclize with two acetylenes, with acetylene and olefins, and with two olefins to form the five-membered ring compounds containing a cobalt atom. The cyclization mechanism with a cobalt cyclopentadienyl compound is shown in Scheme 17.2 [40–44]. The reaction selectively proceeds since the carbon of acetylene bonded with a bulky group bonds to the cobalt atom [45].

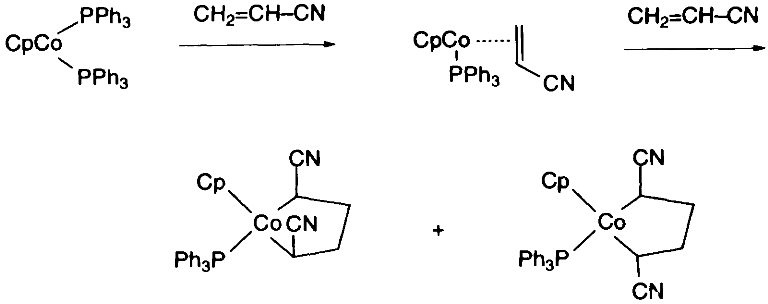
As cyclopentadienyl cobalt compounds are reactive compounds, they are able to react with another acetylene to afford the benzene derivatives as shown in Scheme 17.2.

On the other hand, cyclopentadienylcobalt compounds are substituted by a variety of compounds to afford their derivatives as shown in Scheme 17.3 [40–46].

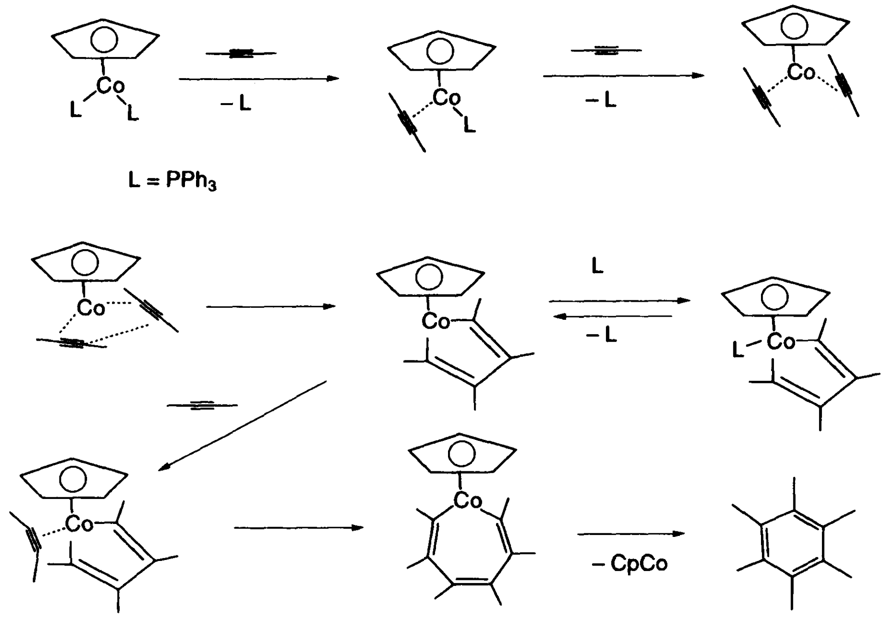
Cyclopentadienylcobalt compounds react with acetylenes and olefins to afford metalacyclopentene as shown in eq. (17.16), and they react with two olefins to afford metalacyclopentane as shown in eq. (17.17) [47,48].



(17.16)



(17.17)



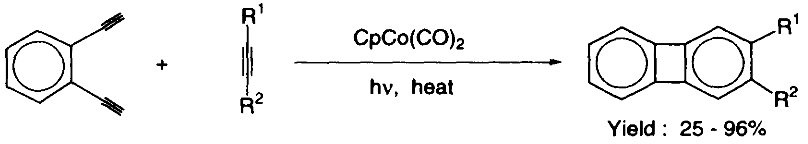
Scheme 17.2 [40–44].

As shown in Scheme 17.4, the cyclopentenecobalt obtained by the reaction of cyclopentadienylcobalt compounds with acetylene and olefins (eq. (17.16)) reacts with acetylene to afford the cyclodiene. However, the cyclopentenecobalt reacts with another olefin to afford the diene complexes by a ring opening reaction since cyclopentadienylcobalt compounds are liable to bond with a diene [49].

The example of the reaction of cyclopentanecobalt with acrylonitrile is shown in eq. (17.17). The structure of the *cis* and *trans* isomers are determined by X-ray diffraction studies [48].

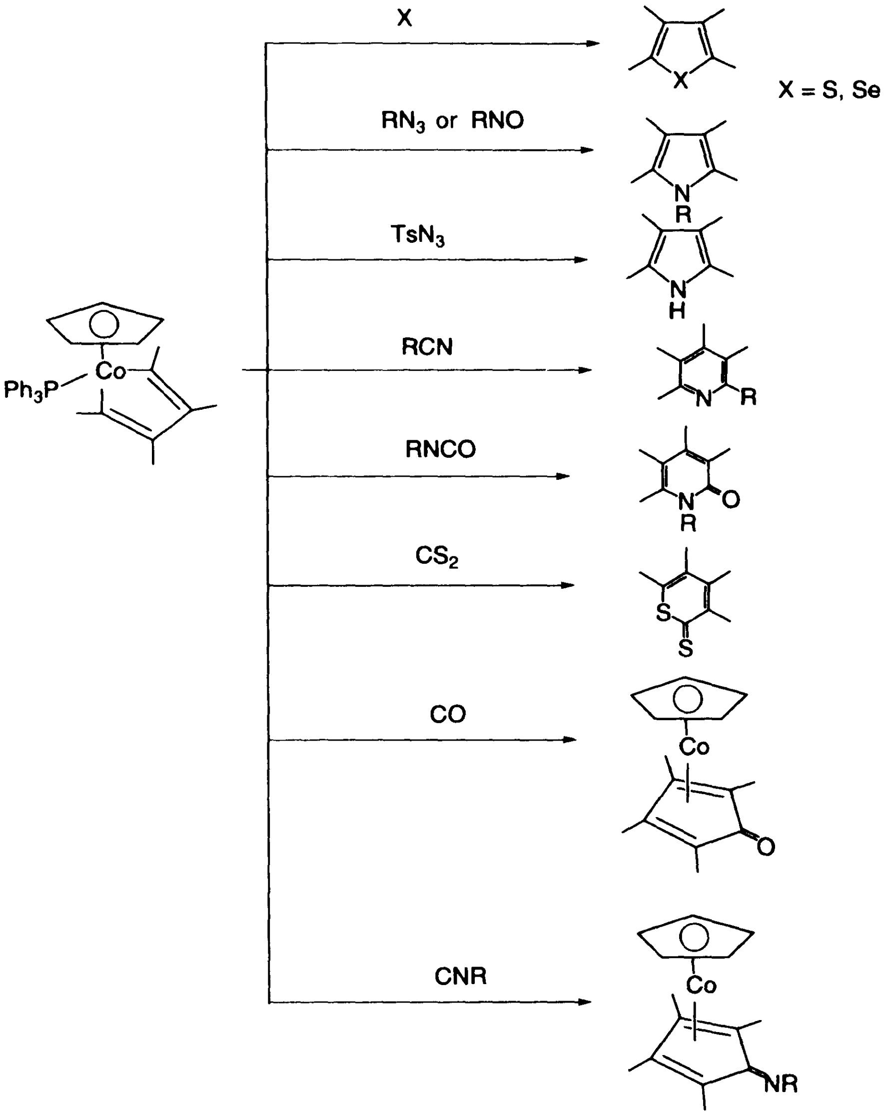
17.5.2 CYCLIZATION OF DIACETYLENES

The formation of a benzene ring with three acetylenes is shown in Scheme 17.2, and the formation of cyclohexadiene with two acetylenes and one olefin is shown in Scheme 17.4. As the cyclization of an α,ω-diacetylene having two triple bonds in one molecule with acetylene or olefin easily proceeds, this cyclization is applied for the syntheses of steroids [40,45,50–56]. The reaction of the α,ω-diacetylene with acetylene affords a biphenylene as shown in eq. (17.18) [50].

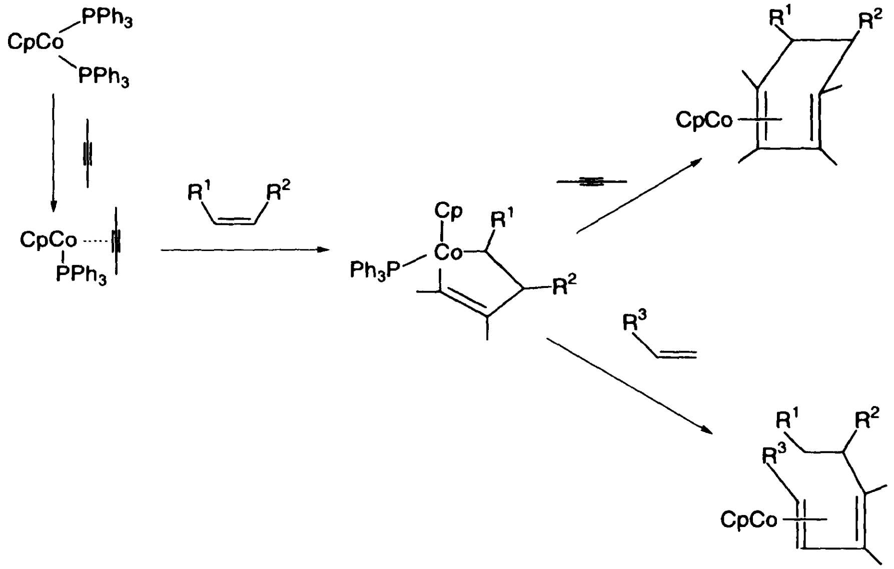


(17.18)

R^1, R^2 = H, n-Bu, C_5H_{11}, Ph, COOMe, $SiMe_3$

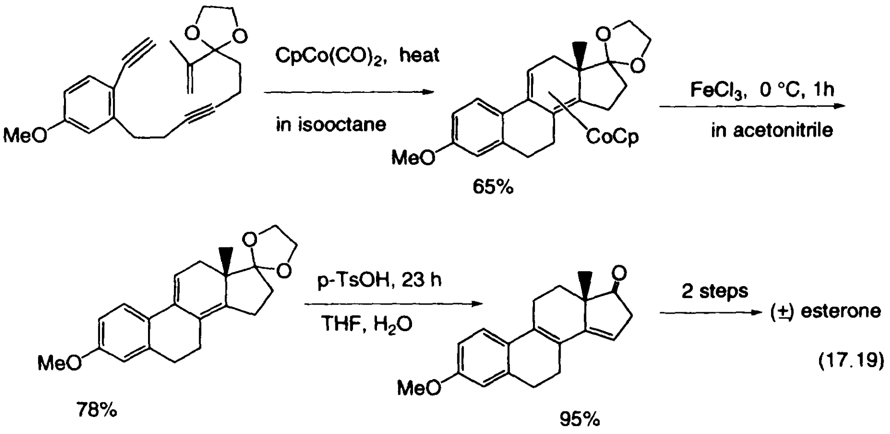


Scheme 17.3 [40].



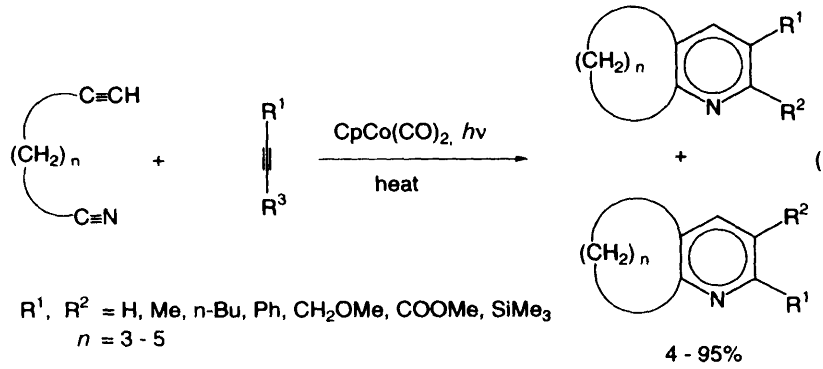
Scheme 17.4 [49].

The cyclization of compounds having two carbon–carbon triple bonds and one carbon–carbon double bond affords a steroid as shown in eq. (17.19) [55].



(17.19)

A cyano group or isocyanate group may be used for the cyclization of a triple bond [40,57]. For example, as shown in eq. (17.20), a reaction with a cyano group affords a pyridine derivative. With the asymmetric acetylene compounds, the carbon bonded with a bulky substituent selectively bonds to the adjacent carbon to nitrogen [57].



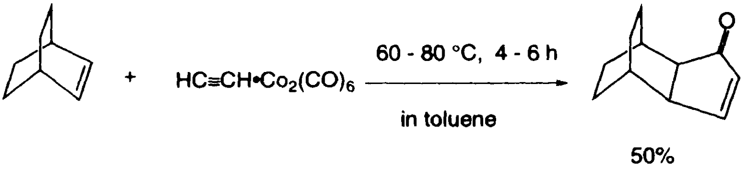
(17.20)

17.5.3 PAUSON–KHAND REACTIONS

The reactions of cyclopentadienylcobalt compounds with two moles of acetylenes afford cobaltcyclopentadienes as shown in Scheme 17.2, and the cobaltcyclopentadienes react with carbon monoxide to afford the η^4-cyclopentadienone as shown in Scheme 17.3.

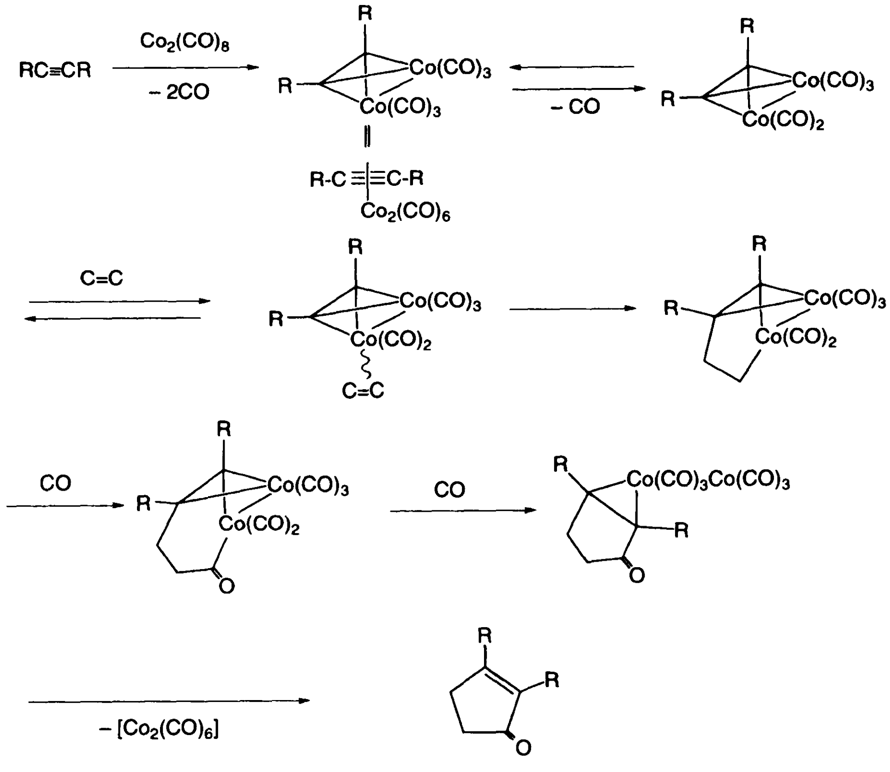
In the Pauson–Khand reaction one acetylene, one olefin and cobaltcarbonyl (as a carbon monoxide source) are used and cyclopentenone is obtained by a $[2+2+1]$ cyclization addition [56–61]. As shown in Scheme 17.5, the Pauson–Khand reaction is, at first, two π-electrons of the reactive acetylene bond to two cobalt atoms (Figure 17.6), then the olefin coordinates to one cobalt atom and then inserts into the cobalt–carbon bond. Further, one carbonyl inserts into the new cobalt–carbon bond, and cyclopentenone is obtained by elimination of $Co_2(CO)_6$ [56].

The Pauson–Khand reaction is, usually, at first, $Co_2(CO)_8$ reacts with acetylene at room temperature for several hours to form a stable acetylene π-complex ($RC{\equiv}CR'{\cdot}Co_2(CO)_6$), then the olefin reacts under a nitrogen or carbon monoxide atmosphere by heating. The yields are 30–60%. The reaction of a bicycloolefin is shown in eq. (17.21) [59].

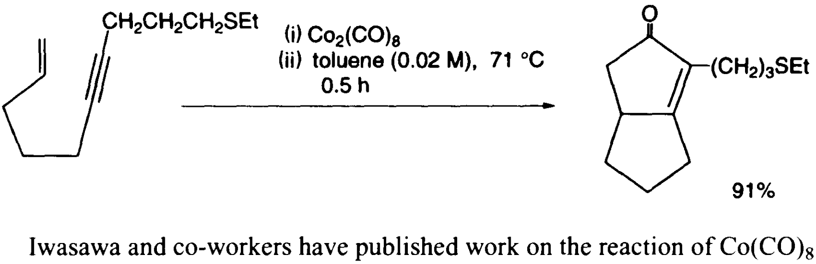


(17.21)

In the compound having a triple and a double bond, generally the intramolecular cyclization of the Pauson–Khand reaction is liable to proceed with a high yield. One example is shown in eq. (17.22) [61].

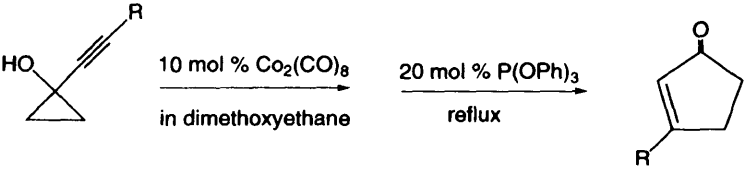


Scheme 17.5 [58].



(17.22)

Iwasawa and co-workers have published work on the reaction of $Co(CO)_8$ with a cyclopropane compound in place of the olefin as shown in eq. (17.23). This is considered to be one modification of the Pauson–Khand reaction [62–64].



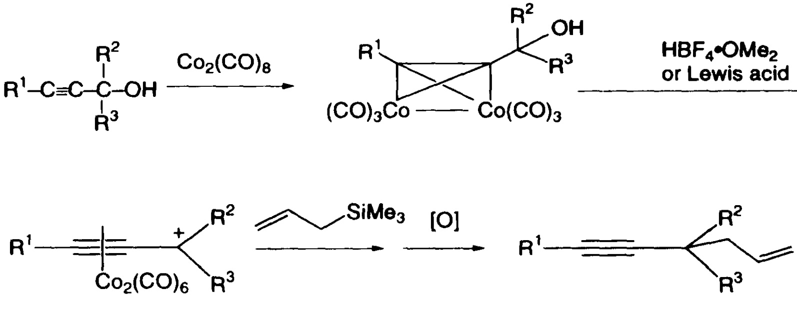
(17.23)

R = Ph, C_6H_{13}, $SiMe_3$, $CH_2OSi(t\text{-}Bu)Me_2$, $CH_2CH_2OSi(t\text{-}Bu)Me_2$

Yield = 61 - 91%

17.5.4 NICOLAS REACTIONS

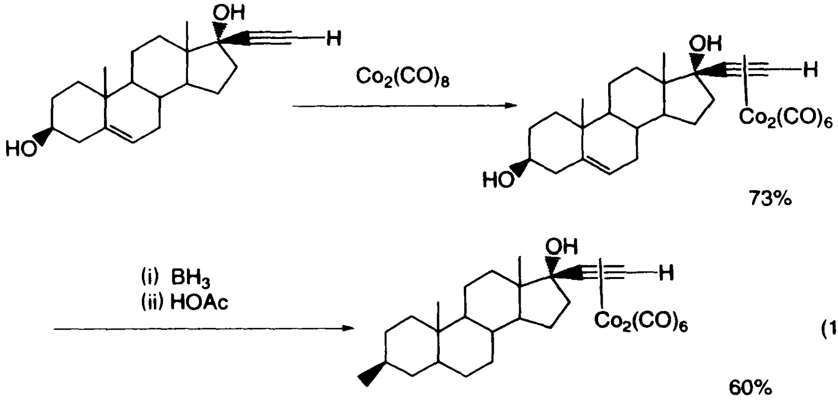
As the cation at the α-position (propargyl position) of acetylene complexes is very stable, the reaction products at the propargyl position with nucleophilic reagents are selectively obtained. Usually, as shown in eq. (17.24), first, the cation is prepared by the reaction of a cobalt complex of propargyl alcohol or propargyl ester with tetrafluoric acid and the nucleophilic reagent reacts with the cation. These reactions are called Nicolas reactions [45,65–67].



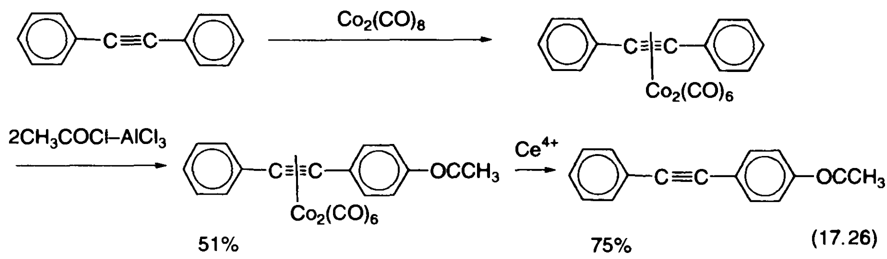
(17.24)

17.5.5 REACTIONS WITH ORGANOCOBALT COMPOUNDS AS THE PROTECTION GROUPS

The Nicolas reaction is that the triple bond coordinates to the cobalt atom, and the triple bond and the carbon atom at the α-position are stabilized. Therefore, with the cobalt compound, the triple bond is stabilized, and the other functional group is able to react. Hence, the cobalt compound is able to be used as the protecting group for a reactive triple bond. For example, the selective reduction of a double bond of a compound having a triple bond and in Friedel–Crafts acylation are shown in eqs. (17.25) and (17.26), respectively [45,68–70].



(17.25)



(17.26)

17.5.6 CARBONYLATIONS

Cobaltcarbonyls are used as catalysts for carbonylations such as hydroformylation (oxo reaction), hydrocarbonylation and amidocarbonylation [70a]. Hydroformylation is the reaction of preparing aliphatic aldehydes in which carbon number is increased by one [46]. Especially, butylaldehyde has been industrially produced largely from propylene: butylaldehyde is used as a raw material for butanol and 2-ethylhexanol, etc. Cobalt and rhodium compounds are used for their catalysts. The reactivity of cobalt catalysts is lower than that of rhodium catalysts. However, more linear products of the reaction shown in eq. (17.27) are obtained. The ratio of

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[100\ ^\circ C,\ 100\ atm]{Co\ or\ Rh} RCH_2CH_2CHO + RCH(CH_3)CHO \quad (17.27)$$

straight-chain obtained with $HCo(CO)_4$ as the cobalt catalyst is 3–4 but the ratio with $HCo(CO)_3(PBu_3)$ as the catalyst is improved to 6–7 [46]. $HCo(CO)_4$ as the hydroformylation catalyst is obtained by the hydrogenation of $Co_2(CO)_8$ (Scheme 17.1) in the reaction system and the active species is thought to be $HCo(CO)_3$ which is formed by decarbonylation by one carbonyl. The reaction is presumed to be as shown in Scheme 17.6 [71–73].

$$RCH{=}CH_2 + HCo(CO)_4 \longrightarrow RCH_2CH_2Co(CO)_4$$

$$RCH_2CH_2Co(CO)_4 \rightleftharpoons RCH_2CH_2COCo(CO)_3$$

$$RCH_2CH_2Co(CO)_4 + CO \longrightarrow RCH_2CH_2COCo(CO)_4$$

$$RCH_2CH_2COCo(CO)_4 + HCo(CO)_4 \longrightarrow RCH_2CH_2CHO + Co_2(CO)_8$$

$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4$$

Scheme 17.6 [71,72].

Hydrocarboxylation is the reaction with water or alcohol in the place of hydrogen in the hydroformylation as shown in eq. (17.27). It produces a carboxylic acid or an ester as shown in eqs. (17.28) and (17.29) [46].

$$\mathrm{RCH{=}CH_2 + CO + H_2O \xrightarrow[CO_2(CO)_8]{140-170\ ^\circ C,\ 100-200\ atm} RCH_2CH_2COOH} \quad (17.28)$$

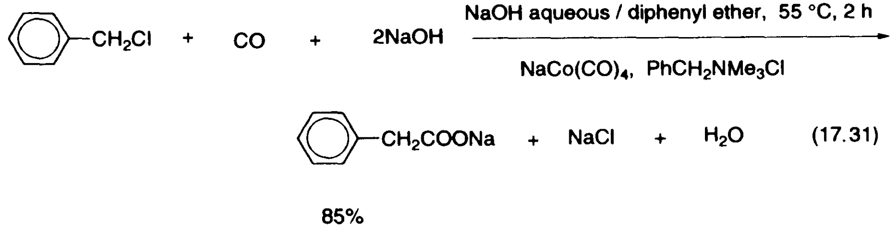
$$\mathrm{RCH{=}CH_2 + CO + R'OH \xrightarrow[CO_2(CO)_8]{80-100\ ^\circ C,\ ca.\ 35\ atm} RCH_2CH_2COOR'} \quad (17.29)$$

In the compounds having two double bonds such as butadiene, the hydrocarboxylation on each double bond proceeds: for example, adipic acid is obtained from butadiene as shown in eq. (17.30). This reaction is noted as the industrial process for adipic acid production [46].

$$\mathrm{CH_2{=}CHCH{=}CH_2 + CO + MeOH \longrightarrow CH_3CH{=}CHCH_2COOMe}$$

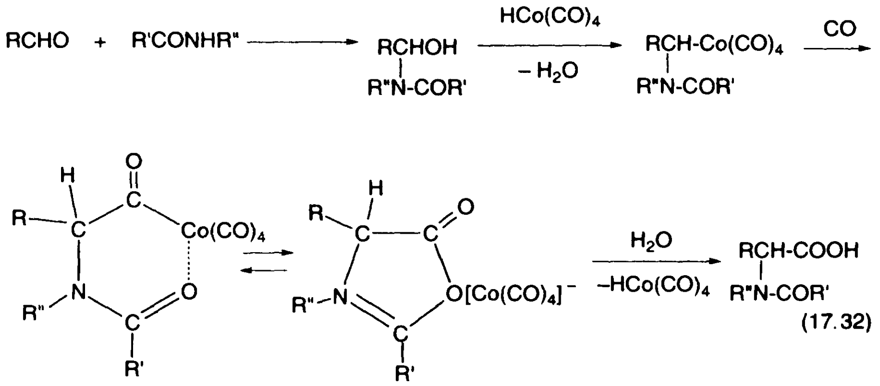
$$\mathrm{CH_3CH{=}CHCH_2COOMe + CO + MeOH \longrightarrow MeOCO(CH_2)_4COOMe} \quad (17.30)$$

Cobaltcarbonyls are used for the carbonylation of benzyl halides or aromatic halides [74–76]. For example, as shown in eq. (17.31), benzylcarboxylic acid is prepared by the reaction of benzyl halide with carbon monoxide. The reaction mechanism is thought to be as follows: at first the halogen atom of the halide is substituted by a cobalt atom and the Co-C bond formed is inserted into by a carbonyl. The phenylacetic acid is industrially produced by using this cobalt catalyst [77]. On aromatic halides, not only monocarbonylation but also double carbonylation is liable to proceed [74,75].



(17.31)

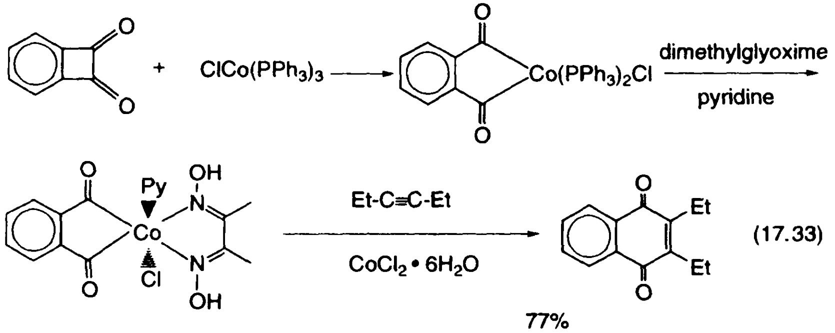
Hydroformylation (oxo reaction) affords aldehyde and an amide is added to the aldehyde under these reaction conditions to produce an acylamino acid as shown in eq. (17.32). This reaction is named the Wakamatsu reaction in which an amino acid is produced directly from an olefin [46,77]. Cobalthydrocarbonyl ($HCo(CO)_4$) is a strong acid as the aldehyde reacts with amide to afford an aminoalcohol, and a dehydration condensation with $HCo(CO)_4$ forms a carbon–Co bond, and carbonylation and hydrolysis to produce the acylamino acid [46,77]. The carbonylation of acetylene shown in Schemes 17.2 and 17.3 affords cyclopentadienone and further, the acetylene carbonylations also afford lactones and quinones [46].



(17.32)

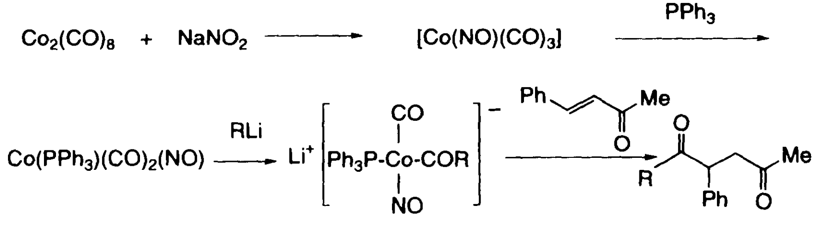
17.5.7 OTHERS

A cobaltphosphine complex ($ClCo(PPh_3)_3$) reacts with cyclobutenedione to afford a phthaloyl cobalt complex. As shown in eq. (17.33), the ligand is exchanged by adding dimethylglyoxime·pyridine, and a quinone is obtained by reaction with acetylene [45,78,79].



(17.33)

The reaction product of cobaltnitrosyl and alkyllithium is used for an acylation agent. For example, as shown in eq. (17.34), an acylation product is obtained in high yield from an α,β-unsaturated ketone by a conjugate addition [45,80].



(17.34)

The Diels–Alder reactions with organocobalt compounds, etc. have been reported as the other reaction with organocobalt compounds [81].

REFERENCES

[1] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
[2] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 4th ed., John Wiley, New York, vol. 6, p. 760, 1993.
[3] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol. A7, p. 281, 1990.
[4] *Kagaku Binran Ooyohen*, Japan Chemical Society, Maruzen, Tokyo, p. 273, 1980.
[5] *Kagaku Daijiten*, Tokyo Kagaku Doojin, Tokyo, p. 808, 1989.
[6] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, 4th ed., p. 452, 1987.
[7] *12093 no Kagaku Shohin*, Kagaku Kogyo Nipposha, p. 91, 1993.
[8] *Sekai Dai Hyakkajiten*, Heibonsha, Tokyo, p. 442, 1992.
[9] Iwao Omea, *Kagaku Kogyo*, **44** (1993) 584, 755, 938.
[10] R.D.W. Kemmitt and D.R. Russell, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 5, p. 1, 1982.
[11] R.B. King, *Organometallic Syntheses, Vol. 1, Transition-Metal Compounds*, Academic Press, New York, 1965.
[12] *Jikken Kagaku Kouza 18, 4th ed., Yuki Kinzoku Sakutai*, Maruzen, Tokyo, p. 295, 1991.
[13] A. Yamamoto ed., *Yuki Kinzoku Kagoubutsu-Gouseiho oyobi Riyouho*, Tokyo Kagaku Dojin, Tokyo, p. 192, 1991.
[13a] A. Misono, *Inorg. Syn.*, **12** (1970) 12.
[13b] A. Sacco and M. Rossi, *Inorg. Syn.*, **12** (1970) 18.
[13c] H.M. Colquhoun, *Acc. Chem. Res.*, **17** (1984) 23.
[13d] A. Yamamoto, S. Kitazume, L.S. Pu and S. Ikeda, *J. Am. Chem. Soc.*, **93** (1971) 371.
[14] J.M. Pratt and P.J. Craig, *Adv. Organomet. Chem.*, **11** (1973) 331.
[15] R.S. Dickson and P.J. Fraser, *Adv. Organomet. Chem.*, **12** (1974) 323.
[16] R.F. Heck, *Adv. Organomet. Chem.*, **4** (1966) 243.
[17] R.B. King and J.J. Eisch, *Organometallic Syntheses*, vol. 3, Elsevier, Amsterdam, 1986.
[18] E.A. McNeil and F.R. Scholer, *J. Am. Chem. Soc.*, **99** (1977) 6243.
[19] P.C. Leung and P. Coppens, *Acta Cryst.*, **B39** (1983) 535.
[20] G.G. Sumner, H.P. Klug and L.E. Alexander, *Acta Cryst.*, **17** (1964) 732.
[21] E. Folga and T. Ziegler, *J. Am. Chem. Soc.*, **115** (1993) 5169.

[22] J.W. Cable, R.S. Nyholm and R.K. Sheline, *J. Am. Chem. Soc.*, **76** (1954) 3373.

[23] R.A. Friedel, I. Wender, S.L. Shufler and H.W. Sternberg, *J. Am. Chem. Soc.*, **77** (1955) 3951.

[24] P.V. Rinze and U. Müller, *Chem. Ber.*, **112** (1979) 1973.

[25] R. Gleiter and G. Pflästerer, *Organometallics*, **12** (1993) 1886.

[26] R. Gleiter and D. Kratz, *Acc. Chem. Res.*, **26** (1993) 311.

[27] G. Winkhaus and G. Wilkinson, *J. Chem. Soc.*, (1961) 602.

[28] Y. Wakatsuki, K. Aoki and H. Yamazaki, *J. Am. Chem. Soc.*, **101** (1979) 1123.

[29] W. Bünder and E. Weiss, *J. Organomet. Chem.*, **92** (1975) 65.

[30] A. Almenningen, E. Gard, A. Haaland and J. Brunvoll, *J. Organomet. Chem.*, **107** (1976) 273.

[31] M.A. Benvenuto, M. Sabat and R.N. Grimes, *Inorg. Chem.*, **31** (1992) 3904.

[32] X. Meng, M. Sabat and R.N. Grimes, *J. Am. Chem. Soc.*, **115** (1993) 6143.

[33] K.W. Piepgrass, M.A. Curtis, X. Wang, X. Meng, M. Sabat and R.N. Grimes, *Inorg. Chem.*, **32** (1993) 2156.

[33a] X. Wang, M. Sabat and R.N. Grimes, *J. Am. Chem. Soc.*, **116** (1994) 2687.

[34] R.F. Heck and D.S. Breslow, *J. Am. Chem. Soc.*, **83** (1961) 1097.

[35] W.R. McClellan, H.H. Hoehn, H.N. Cripps, E.L. Muetterties and B.W. Howk, *J. Am. Chem. Soc.*, **83** (1961) 1601.

[36] M. Bottrill, R. Goddard, M. Green and P. Woodward, *J. Chem. Soc. Dalton Trans.*, (1979) 1671.

[37] W.G. Sly, *J. Am. Chem. Soc.*, **81** (1959) 18.

[37a] K.H. Zimmermann, R.S. Pilato, I.T. Horváth and J. Okuda, *Organometallics*, **11** (1992) 3935.

[38] R.F. Heck and D.S. Breslow, *J. Am. Chem. Soc.*, **84** (1962) 2499.

[39] P. Jutzi, M.O. Kristen, J. Dahlhaus, B. Neumann and H.-G. Stammler, *Organometallics*, **12** (1993) 2980.

[39a] T. Janecki, P.L. Pauson and A. Pietrzykowski, *J. Organomet. Chem.*, **325** (1987) 247.

[40] K.P.C. Vollhardt (translator: H. Yamazaki), *Kagaku Zokan*, **105** (1985) 165.

[41] A.H. Janowicz, H.E. Bryndza and R.G. Bergman, *J. Am. Chem. Soc.*, **103** (1981) 1516.

[42] H. Yamazaki and N. Hagihara, *J. Organomet. Chem.*, **21** (1970) 431.

[43] H. Yamazaki and Y. Wakatsuki, *J. Organomet. Chem.*, **139** (1977) 157.

[43a] Y. Wakatsuki, O. Nomura, K. Kitaura, K. Morokuma and H. Yamazaki, *J. Am. Chem. Soc.*, **105** (1983) 1907.

[44] D.R. McAlister, J.E. Bercaw and R.G. Bergman, *J. Am. Chem. Soc.*, **99** (1977) 1666.

[45] *Jikken Kagaku Kouza 25, 4th ed., Yuki Gousei VII*, Maruzen, Tokyo, p. 331, 1991.

[46] *Yuki Kinzoku no Kagaku, Shinkagaku Library*, Japan Chemical Society ed., Dai Nippon Tosho, Tokyo, 1989.

[47] Y. Wakatsuki and H. Yamazaki, *J. Chem. Soc. Chem. Commun.*, (1980) 1270.

[48] Y. Wakatsuki, T. Sakurai and H. Yamazaki, *J. Chem. Soc. Dalton Trans.*, (1982) 1923.

[49] Y. Wakatsuki, K. Aoki and H. Yamazaki, *J. Am. Chem. Soc.*, **101** (1979) 1123.

[50] B.C. Berris, Y.-H. Lai and K.P.C. Vollhardt, *J. Chem. Soc. Chem. Commun.*, (1982) 953.

[51] R.L. Hillard III and K.P.C. Vollhardt, *J. Am. Chem. Soc.*, **99** (1977) 4058.

[52] K.P.C. Vollhardt, *Acc. Chem. Res.*, **10** (1977) 1.

[53] R.L. Funk and K.P.C. Vollhardt, *J. Am. Chem. Soc.*, **102** (1980) 5253.

[54] J.-C. Clinet, E. Duñach and K.P.C. Vollhardt, *J. Am. Chem. Soc.*, **105** (1983) 6710.

[55] E.D. Sternberg and K.P.C. Vollhardt, *J. Org. Chem.* **47** (1982) 3447.

[56] E.D. Sternberg and K.P.C. Vollhardt, *J. Org. Chem.*, **49** (1984) 1574.

[57] D.J. Brien, A. Naiman and K.P.C. Vollhardt, *J. Chem. Soc. Chem. Commun.*, (1982) 133.

[58] N.E. Schore, *Organic Reaction*, **40** (1991) 1.

[59] N.E. Schore, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 5, p. 1037, 1982.

[60] P.L. Pauson, *Tetrahedron*, **41** (1985) 5855.

[61] M.E. Krafft, I.L. Scott, R.H. Romero, S. Feibelmann and C.E. Van Pelt, *J. Am. Chem. Soc.*, **115** (1993) 7199.

[62] N. Iwasawa and T. Matsuo, *Chem. Lett.*, (1993) 997.

[63] N. Iwasawa and M. Iwamoto, *Chem. Lett.*, (1993) 1257.

[64] N. Iwasawa, *Chem. Lett.*, (1992) 473.

[65] K.M. Nicholas, *Acc. Chem. Res.*, **20** (1987) 207.

[66] R.F. Lockwood and K.M. Nicholas, *Tetrahedron Lett.*, (1977) 4163.

[67] K.M. Nicholas and J. Siegel, *J. Am. Chem. Soc.*, **107** (1985) 4999.

[68] K.M. Nicholas and R. Pettit, *Tetrahedron Lett.*, (1971) 3475.

[69] C. Mukai, K. Nagami and M. Hanaoka, *Tetrahedron Lett.*, (1989) 5623.

[70] D. Seyferth and A.T. Wehman, *J. Am. Chem. Soc.*, **92** (1970) 5520.

[70a] A. Matsuda, *Yuki Gosei Kagaku Kyokaishi*, **36** (1987) 173.

[71] A.N. Chalk and J.F. Harrod, *Adv. Organomet. Chem.*, **6** (1968) 119.

[72] T. Ziegler, L. Cavallo and A. Bérces, *Organometallics*, **12** (1993) 3586.

[73] A.E.S. Miller and J.L. Beauchamp, *J. Am. Chem. Soc.*, **113** (1991) 8765.

[74] L. Cassar and M. Foa, *J. Organomet. Chem.*, **134** (1977) C15.

[75] T. Kashimura, K. Kudo, S. Mori and N. Sugita, *Chem. Lett.*, (1986) 483.

[76] M. Miura, F. Akase and M. Nomura, *J. Org. Chem.*, **52** (1987) 2623.

[77] J. Tsuji, *Yuki Gosei okaeta Sen-i Kinzoku, sono Kihonteki Rikai to Katsuyouho*, Kagaku Dojin, Tokyo, 1991.

[78] L.S. Liebeskind, S.L. Baydon, M.S. South, S. Iyer and J.P. Leeds, *Tetrahedron*, (1985) 5839.

[79] L.S. Liebeskind, R. Chidambaram, D. Mitchell and B.S. Foster, *Pure Appl. Chem.*, **60** (1988) 27.

[80] L.S. Hegedus and R.J. Perry, *J. Org. Chem.*, **50** (1985) 4955.

[81] T.L. Smalley, Jr., M.W. Wright, S.A. Garmon, M.E. Welker and A.L. Rheingold, *Organometallics*, **12** (1993) 998.

18 Organorhodium Compounds

18.1 INTRODUCTION

Rhodium is an element which is widely utilized as a catalyst for the treatment apparatus of car waste gas which caused public attention recently, and as the catalyst in the production of various kinds of chemicals. In the studies of organo-transition metal chemistry, recently, many articles on the element together with palladium have been reported.

18.2 RHODIUM

Rhodium belongs to group 9 of the periodic table (the same as cobalt), and the outer electronic configuration is $4d^8 5s^1$. It exists as 0.0002 ppm in the Earth's crust [1]. Rhodium is produced similarly to ruthenium described in Chapter 16 from mainly anode slime in the electrolytic refining of crude copper or crude nickel obtained from sulfide ores. The anode slime containing the precious elements is treated with aqua regia to separate platinum, palladium and gold as the insoluble chloro complexes, soluble silver and lead are separated by treatment with PbO as a fusing agent and with nitric acid, and insoluble ruthenium, iridium and osmium are separated by fusing with $NaHSO_4$. The residual solution is treated with NaOH, HCl, $NaNO_2$, NH_4Cl and HCl to form $(NH_4)_3RhCl_6$ and this is reduced with hydrogen at high temperatures to produce rhodium [1,2].

Rhodium is the whitest metal in the platinum group metals and it does not lose its luster under any atmospheres at ordinary temperatures. When rhodium is heated, the protective coating of rhodium oxide forms at 700°C. Further, at 1100°C the oxide is dissociated to rhodium and oxygen. Rhodium dissolves in hot sulfuric acid or in aqua regia. Rhodium reacts with a halogen at high temperatures to afford a trihalide [1–6]. Rhodium has a high reflexibility and is used as a reflex mirror. The alloy with rhodium is used in thermocouples, crucibles, catalysts, electrical contact points, heat-resistant materials, corrosion resistant materials, etc.

Rhodium is used as catalysts for waste gas treatment in cars, hydrogenation, hydroformylation, etc. [1–6]. The properties of rhodium are shown in Table 18.1.

Table 18.1 Properties of rhodium [1,2]

Property	Value
melting point, °C	1960
boiling point, °C	3760
crystal structure	face-centered cubic
density, 20°C, g/cm^3	12.41
specific heat at 0°C, J g^{-1}	0.247
linear coefficient of thermal expansion at 20°C, K^{-1}	8.3×10^{-6}
electrical resistivity at 20°C, μΩ·cm	4.5
hardness	
Mohs scale	6
Vickers hardness, annealed	120
thermal conductivity, Wm^{-1}K^{-1}	150.6
mass susceptibility, cm^{3}g^{-1}	0.99×10^{-6}

18.3 PREPARATION OF ORGANORHODIUM COMPOUNDS

Organorhodium compounds are prepared by similar methods to the preparation methods of organoruthenium compounds described in Chapter 16.

(1) Carbonylations
(2) Reactions with rhodiumcarbonyls
(3) Reactions with unsaturated compounds
(4) Reactions with cyclopentadienyl compounds
(5) Others

18.3.1 CARBONYLATIONS

Metal halides are used as the starting materials of the synthesis of organorhodium compounds similar to the synthesis of organoiron compounds and organoruthenium compounds. Metal carbonyls ($M_m(CO)_n$) are prepared by carbonylation of the metal halides, and the metal halides are often used as starting materials for organometallic compounds. However, rhodiumcarbonyls, such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ described below, form relatively stable clusters and the reactivity is not so high as the organoiron compound ($Fe(CO)_5$) or organoruthenium compound ($Ru_3(CO)_{12}$). Thus, $[RhCl(CO)_2]_2$ is used as the basic raw material for organorhodium compounds.

$Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are prepared by the reaction of rhodium chloride with carbon monoxide. $Rh_6(CO)_{16}$ decomposes at 200°C under a nitrogen atmosphere. $Rh_6(CO)_{16}$ is stable in air, but it gradually decomposes on being stored at room temperature for a long time. It should be stored under a carbon monoxide atmosphere. $Rh_4(CO)_{12}$ decomposes at 130–140°C under a nitrogen atmosphere to afford $Rh_6(CO)_{16}$ [7–15]. Hence, $Rh_6(CO)_{16}$ is more stable than $Rh_4(CO)_{12}$. But the solubility of $Rh_6(CO)_{16}$, is low and it dissolves only in dichloromethane and chloroform. As $Rh_4(CO)_{12}$ dissolves in common organic solvents such as pentane, toluene, tetrahydrofuran, acetone and methyl alcohol, it is easy to perform reactions with many compounds. Hence, $Rh_4(CO)_{12}$ is preferably used as the raw material for organorhodium compounds compared with $Rh_6(CO)_{16}$. $Rh_4(CO)_{12}$ is prepared by the reaction of rhodium chloride with carbon monoxide in the presence of a copper catalyst at room temperature as shown in eq. (18.1). As a small amount of $Rh_6(CO)_{16}$ forms in this reaction, pure $Rh_4(CO)_{12}$ is obtained by the extraction of the reaction product with pentane under a carbon monoxide atmosphere [7,8].

$$RhCl_3 + 2Cu + 4CO + NaCl \xrightarrow{\text{room temp}} Na[RhCl_2(CO)_2] + 2Cu(CO)Cl$$

$$4Na[RhCl_2(CO)_2] + 6CO + 2H_2O \longrightarrow \underset{80-90\ \%}{Rh_4(CO)_{12}} + 2CO_2 + 4NaCl + 4HCl \quad (18.1)$$

$Rh_6(CO)_{16}$ is prepared by the reaction of tetraacetatedirhodium with carbon monoxide on heating as shown in eq. (18.2) [7].

$$3Rh_2(OCOCH_3)_4 + 22CO + 6H_2O \xrightarrow[\ ]{\substack{75-80\ ^\circ C \\ 20\ h}} \underset{87\ \%}{Rh_6(CO)_{16}} + 6CO_2 + 12CH_3COOH \quad (18.2)$$

The carbonylation of two chlorine atoms of the three chlorine atoms of rhodium chloride easily proceeds. As shown in eq. (18.3), rhodium chloride reacts with carbon monoxide in the absence of a catalyst to afford easily sublimable $[RhCl(CO)_2]_2$ in high yield [7,16].

$$2RhCl_3{\bullet}3H_2O + 6CO \xrightarrow{100\ ^\circ C,\ 3-5\ h} \underset{\substack{\text{mp } 126.5-127\ ^\circ C \\ 96\ \%}}{[RhCl(CO)_2]_2} + 6H_2O + 2COCl_2 \quad (18.3)$$

$[RhCl(CO)_2]_2$ is a compound having two bridge structures with its chlorine atoms (see Figure 18.6). Thus the bridge structure is liable also to form with unsaturated hydrocarbons such as dienes described in the following section. For example, the chloro-bridged structure of the diene as shown in eq. (18.4), reacts reversibly with carbon monoxide accompanied by the ligand exchange reaction of diene and carbonyl groups [7].

$$Rh_2Cl_2(diene)_2 + 4CO \xrightleftharpoons[\text{in hexane}]{} \underset{65-75\ \%}{[RhCl(CO)_2]_2} + 2diene \quad (18.4)$$

diene = 1,5-cyclooctadiene, norbornadiene

As $[RhCl(CO)_2]_2$ is the intermediate of the carbonylation of rhodium chloride, as shown in eqs. (18.5) and (18.6), $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are prepared by further carbonylation with mild reaction conditions [9,10].

$$[RhCl(CO)_2]_2 \xrightarrow[\text{in hexane}]{\text{CO, 1 atm, room temp, 3 - 3.5 h , NaHCO}_3} \underset{55-60\ \%}{[Rh_4(CO)_{12}]} \quad (18.5)$$

$$[RhCl(CO)_2]_2 \xrightarrow[\text{MeOH, H}_2\text{O(5 \%)}]{\text{CO, 1 atm, room temp, 2 - 3 days, LiOAc}} \underset{80-90\ \%}{[Rh_6(CO)_{16}]} \quad (18.6)$$

When formaldehyde reacts with rhodium halides, carbonylation proceeds (hydrocarbonylation between formaldehyde and a ruthenium halide as described in Chapter 16 proceeds). A Vaska type rhodium complex is obtained by the reaction with phosphine as shown in eq. (18.7) [17].

$$RhCl_3{\bullet}3H_2O \quad + \quad 2PPh_3 \xrightarrow{\text{HCHO (37 \%)}} \underset{85\ \%}{RhCl(CO)(PPh_3)_2} \quad (18.7)$$

The rhodiumphosphinecarbonyl complex affords $RhH(CO)(PPh_3)_3$ by reduction with $NaBH_4$ in the presence of phosphine as shown in eq. (18.8) [18]. The phosphinecarbonylhydride is also prepared by the reduction of rhodium halides with $NaBH_4$ [18] or with KOH in the presence of formaldehyde as shown in eqs. (18.9) and (18.10).

$$RhCl(CO)(PPh_3)_2 \ + \ PPh_3 \xrightarrow[\text{in EtOH}]{\text{NaBH}_4\text{, reflux}} \underset{90\ \%}{RhH(CO)(PPh_3)_3} \quad (18.8)$$

$$RhCl_3{\bullet}3H_2O + 3PPh_3 + HCHO \xrightarrow[\text{in EtOH}]{\text{NaBH}_4} \underset{72\ \%}{RhH(CO)(PPh_3)_3} \quad (18.9)$$

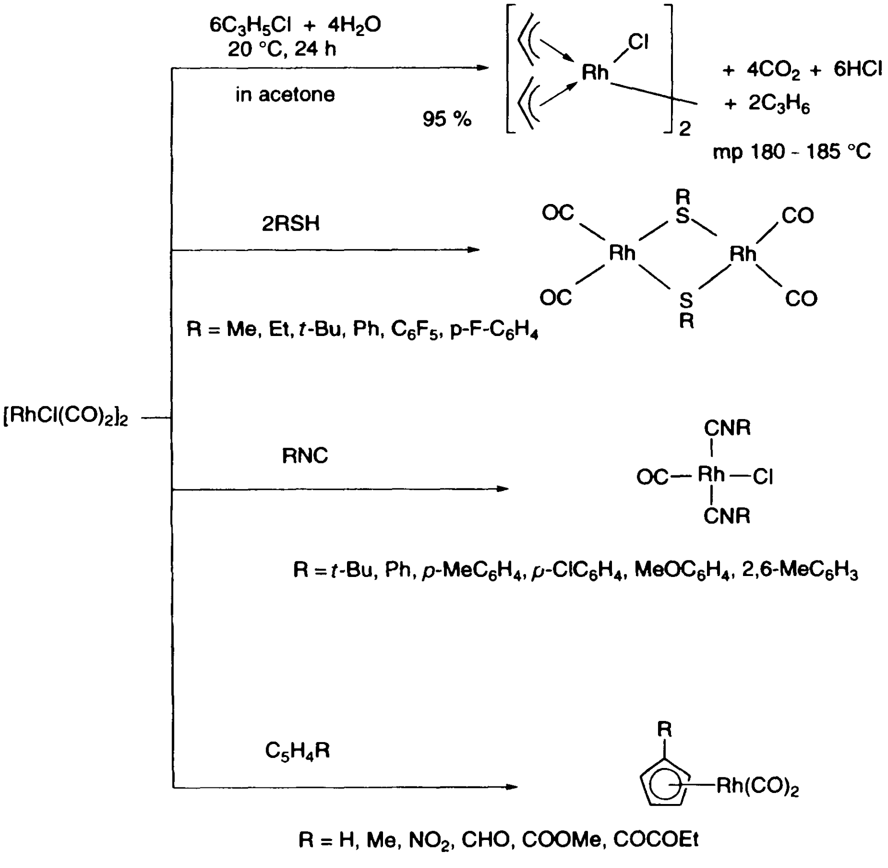
$$RhCl_3{\bullet}3H_2O + 3PPh_3 + HCHO \xrightarrow[\text{in EtOH}]{\text{KOH, reflux, 10 min}} \underset{94\ \%}{RhH(CO)(PPh_3)_3} \quad (18.10)$$

18.3.2 REACTIONS WITH RHODIUMCARBONYLS

Rhodiumcarbonyls such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$, form stable clusters as described below, and their reactivities are low compared to ironcarbonyl ($Fe(CO)_5$) and rutheniumcarbonyl ($Ru_3(CO)_{12}$). $[RhCl(CO)_2]_2$ is available as the raw material for the synthesis of organorhodium compounds. $[RhCl(CO)_2]_2$ is a stable red crystal. A highly pure crystal is easily obtained by sublimation. $[RhCl(CO)_2]_2$ reacts easily with various compounds as shown in Scheme 18.1 [7,19,20].

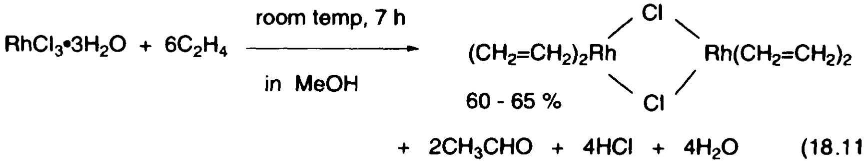
18.3.3 REACTIONS WITH UNSATURATED COMPOUNDS

Rhodium compounds are liable to be coordinated by unsaturated compounds and easily react with unsaturated compounds such as monoolefins and dienes. For example, reactions with ethylene, cyclooctene and 1,5-cyclooctadiene are shown in eqs. (18.11) [21–23], (18.12) [7] and (18.13) [7], respectively [7,24,25]. The



Scheme 18.1 [7,19,20]

reaction with 1,5-cyclooctadiene as shown in eq. (18.13) is the similar reverse reaction of that shown in eq. (18.4).



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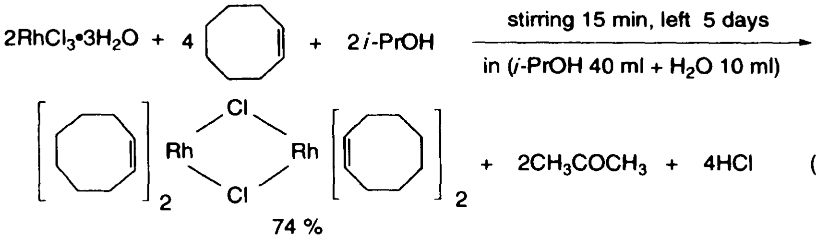

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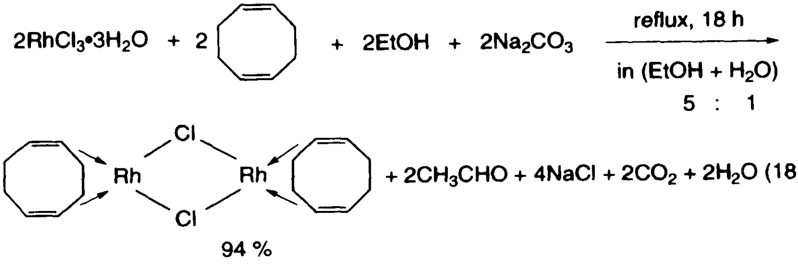


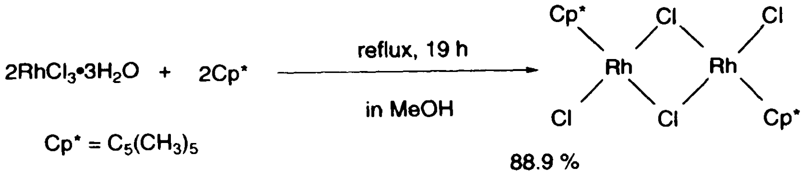
(18.13)

Recently, fullerene reacts with an ethylenerhodium compound ((C_2H_2)$_2$ Rh(acac)) to afford the fullerene π-complex of rhodium by the ligand exchange reaction of ethylene with one carbon–carbon double bond of fullerene. The pyridine derivatives (C_{60}Rh(3,5-Me-py)(acac)) is isolated and the structure is determined by X-ray diffraction studies [26].

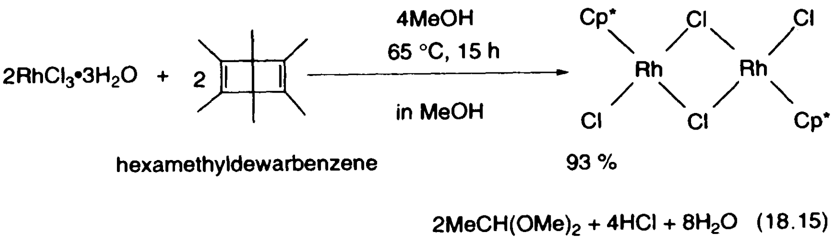
18.3.4 REACTIONS WITH CYCLOPENTADIENYL COMPOUNDS

As the organorhodium compound of dipentadienylmetal compounds (Cp_2M), similar to ferrocene, is a 19-electron compound, it is similar to the cobalt compound (Cp_2Co), and is not stable. Hence, Cp_2Rh is not available to be used as the raw material of the synthesis of organorhodium compounds. The representative cyclopentadienylrhodium compound is [Cp*RhCl]$_2$ which is prepared by the reaction of pentamethylcyclopentadiene with rhodium chloride as shown in eq.

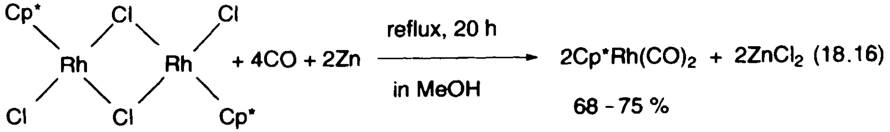
(18.14). These compounds are also obtained by the rearrangement reaction of hexamethyldewarbenzene as shown in eq. (18.15) [7,27,28].



(18.14)



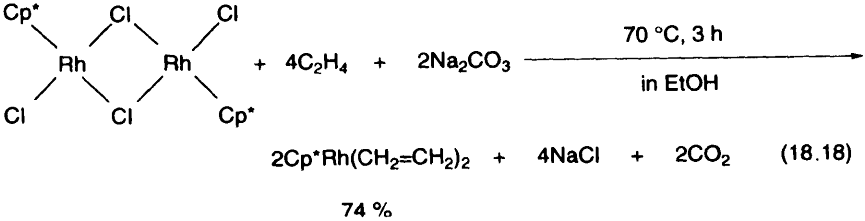
Since the bond between strong electron-donating pentamethylcyclopentadienyl and rhodium is strong, the reaction with carbon monoxide affords Cp*Rh(CO)$_2$ by the fission of the chloro-bridged bond as shown in eq. (18.16).



CpRh(CO)$_2$ (Cp*Rh(CO)$_2$) and CpRh(PPh$_3$)$_2$ [29] are obtained from a Wilkinson complex as shown in eq. (18.17), and are also used as raw material for the synthesis of organorhodium compounds [7]. The reaction as shown in eq. (18.17) yields a benzene complex (CpRh(PPh$_3$)$_2$·C$_6$H$_6$). However, benzene is able to be removed by heating at 140°C under reduced pressure [29].

$$\mathrm{RhCl(PPh_3)_3} + \mathrm{CpNa} \xrightarrow[\text{in (THF + C}_6\text{H}_6\text{))} \atop 1\ :\ 1]{\text{room temp, 30 min}} \mathrm{CpRh(PPh_3)_2} \qquad (18.17)$$

A reaction between [Cp*RhCl$_2$]$_2$ and ethylene is shown in eq. (18.18) [17]. The reaction proceeds by ligand exchange reaction of ethylene with a bridged chlorine atom.

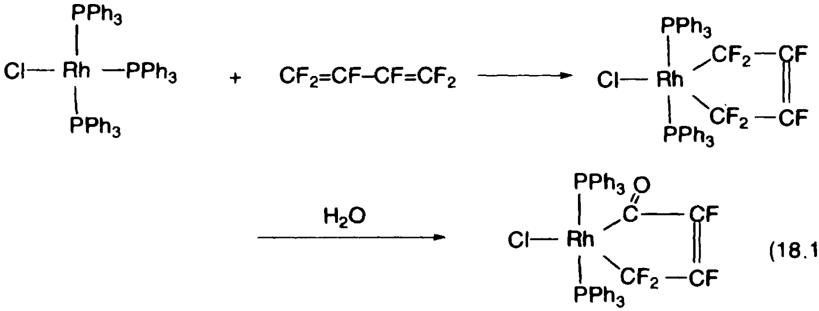


(18.18)

18.4 STRUCTURES OF ORGANORHODIUM COMPOUNDS

Rhodium tends to bond with a compound having nine electrons to satisfy the 18-electron rule. Hence, Cp_2Rh in which Rh bonded with two cyclopentadienyl rings is not stable, and cyclopentadienylrhodium is liable to bond with two olefins or with a diene as shown in Figure 18.1. These structures are determined by X-ray diffraction studies [30–33].

The Wilkinson complex ($RhCl(PPh_3)_3$) has the square planar structure of four coordination [34] and is well known as a homogeneous hydrogenation catalyst. The Wilkinson complex reacts with hexafluorobutadiene to afford the metallacyclopentene of five-coordination and since this is a 17-electron compound, it is labile and is liable to be hydrolyzed as shown in eq. (18.19). However, a reaction with trimethylphosphinerhodium in the place of the Wilkinson complex having bulky triphenylphosphine, forms an 18-electron compound, since it is able to form a six-coordination compound and is stable to water. The structure is determined by X-ray diffraction studies [35].



(18.19)

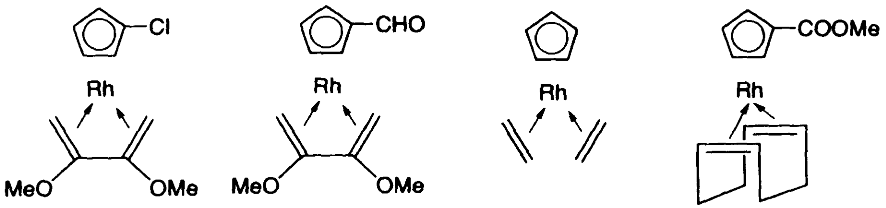
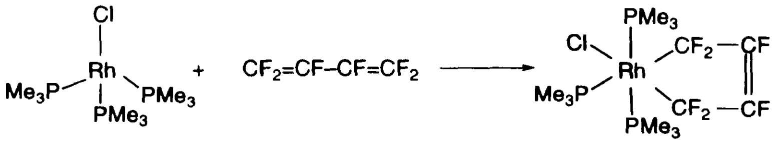
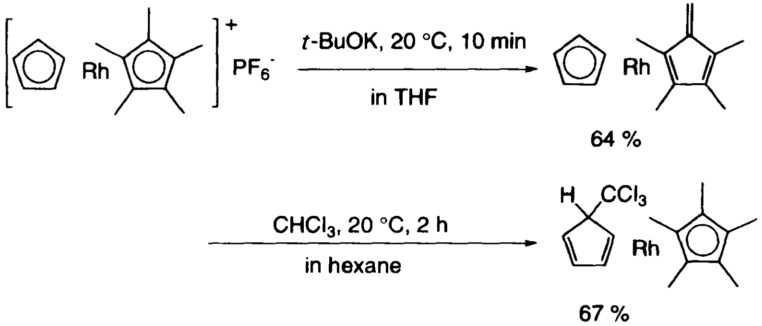


Figure 18.1 Organorhodium compounds coordinated by η^5-cyclopentadienide and diene or two olefins [30–33].



(18.20)

$[CpCp^*Rh]^+PF_6^-$ easily affords 18-electron compounds by a reduction with alkali. The 18-electron compound changes to another 18-electron compound by the addition of chloroform to a cyclopentadienyl ring as shown in eq. (18.21) [36].



(18.21)

[Bis(pyrazolyl)borate]rhodium is a square planar structure 17-electron compound by the coordination of two double bonds and two pyrazolyl groups. Hence it is liable to be coordinated with another ligand and it has a high affinity to hydrogen. This compound forms an agostic bond (three-center two-electron bond) to one hydrogen of 9-BBN (9-borabicyclo[3.3.1]nonane) as shown in Figure 18.2 [37].

A rhodium nitrogen complex displays a square planar four-coordination structure and the nitrogen molecule forms a side-on bond as shown in Figure 18.3 [38,39]. Oxygen and acetylene complexes also form the side-on bond [39].

The structures of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are shown in Figures 18.4 and 18.5, respectively [40,41]. These compounds form cluster structures in which rhodium atoms bond each other. These consist of Rh–Rh bond, Rh–CO bond and a bridged carbonyl bond in which the carbon of carbonyl group bonds to two or three rhodium atoms. As $Rh_6(CO)_{16}$ has more Rh–Rh bonds compared with $Rh_4(CO)_{12}$, it is more stable and has less solubility.

The structure of $[RhCl(CO)_2]_2$ is shown in Figure 18.6 [42]. Two chlorine atoms form a bridge structure, and each rhodium atom forms the square planar of four-coordination with two chlorine atoms and two carbonyl groups. Two planar $Rh(CO)_2Cl_2$ groups intersect at an angle of 124°. The resulting dimers apparently are linked by direct Rh–Rh bonds to form infinite chains. Then rhodium is considered to form the octahedral structure of six-coordination. The Rh–Rh bond length is 3.31 Å and it is much longer than that (2.73 Å, 2.776 Å) of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$. Hence, $[RhCl(CO)_2]_2$ is more reactive compared with those of the rhodiumcarbonyl cluster.

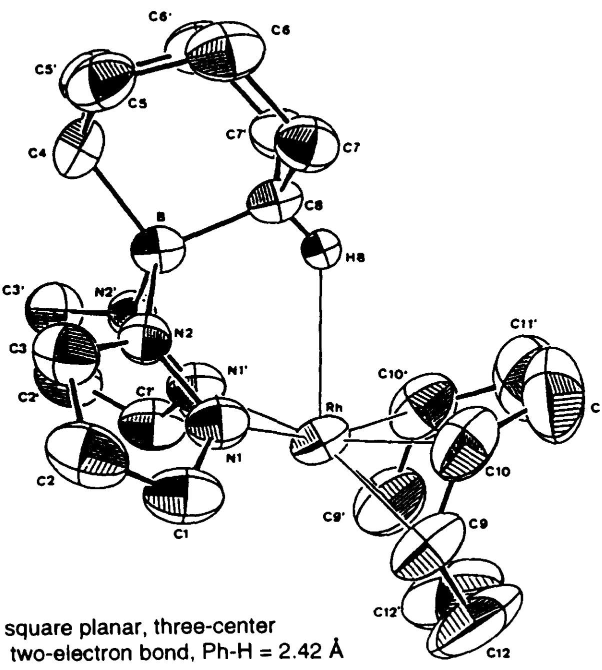


Figure 18.2 Molecular structure of [(cyclooctane-1,5-diyl)bis(pyrazol-1-yl)borato][1,5-cyclooctadiene]rhodium [37].

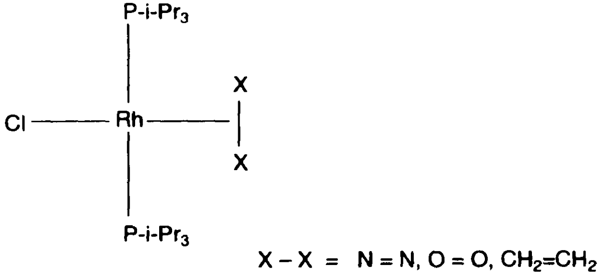
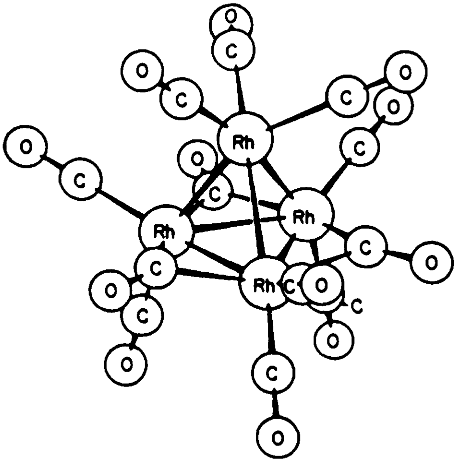
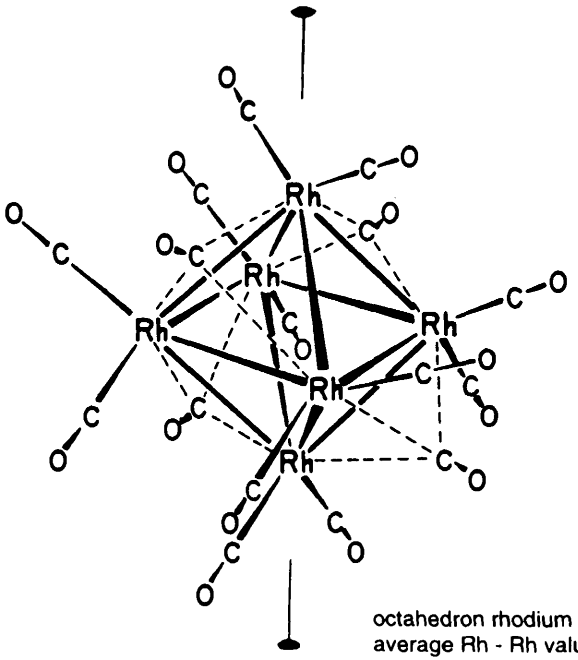


Figure 18.3 Structure of trans-chloro(dinitrogen)-, chloro(dioxygen)-, and chloro-(ethylene)-bis(tri-isopropylphosphine)rhodium [39].



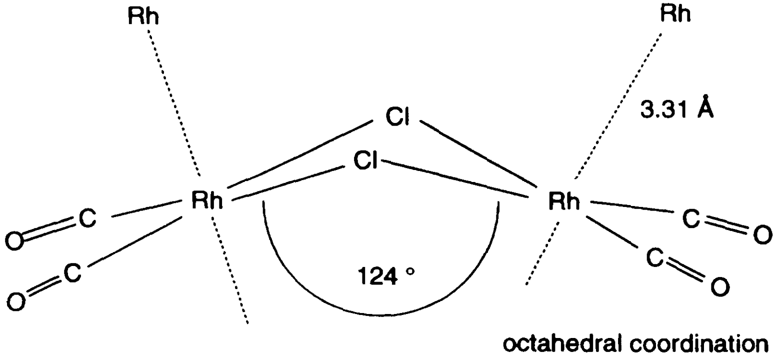
tetrahedron rhodium atoms, average Rh-Rh value = 2.73Å

Figure 18.4 Molecular structure of tetrarhodium dodecacaronyl [40].



octahedron rhodium atoms,
average Rh - Rh value = 2.776 Å

Figure 18.5 Molecular structure of $Rh_6(CO)_{16}$ [41].



two essentially planar RhCl(CO)$_2$ groups intersect at an angle of 124 °

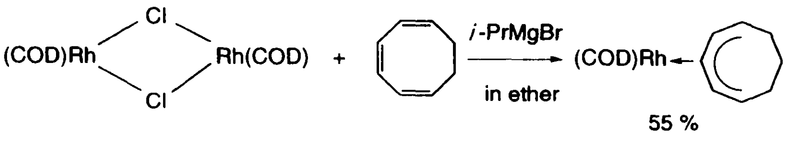
Figure 18.6 Molecular structure of $[RhCl(CO)_2]_2$ [42].

$[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$ forms two chloro-bridges and the other two chlorine atoms form σ-bonds and these four chlorine atoms are located in each of the three legs of two stools. These form two three-legged piano-stool structures as shown in Figure 18.7 [43].

Recently, the sandwich structure of $(\eta^5\text{-}C_5HPh_4)_2Rh$ and the half sandwich structure of $(\eta^5\text{-}C_5H_5)RhCOD$ have been determined by X-ray diffraction studies [43a,43b].

18.5 REACTION OF ORGANORHODIUM COMPOUNDS

$[RhCl(CO)_2]_2$, $Rh_4(CO)_{12}$, $[CpRhCl_2]_2$, $CpRh(CO)_2$ and $[(diene)RhCl]_2$ are used as the raw material of the synthesis of organorhodium compounds described above, and these reactions are liable to proceed by the fission of bridged-halogen bond and by the ligand exchange reaction of carbonyl groups. 1,5-Cyclooctadiene is usually used as the dienes of $[(diene)RhCl]_2$. As the bond between 1,5-cyclooctadiene and rhodium of $[(COD)RhCl]_2$ is stable, the reaction with various unsaturated hydrocarbons proceeds by ligand exchange reaction with the fission of the halo-bridged bond. For example, the reaction of $[(COD)RhCl]_2$ with 1,3,5-cyclooctatriene is shown in eq. (18.22) [44].



(18.22)

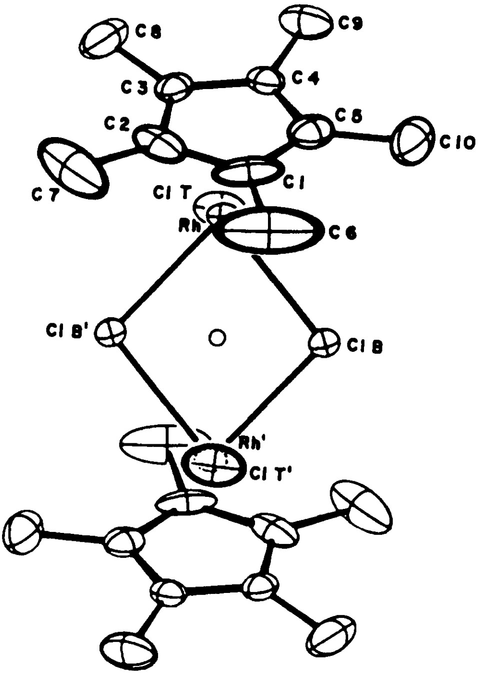
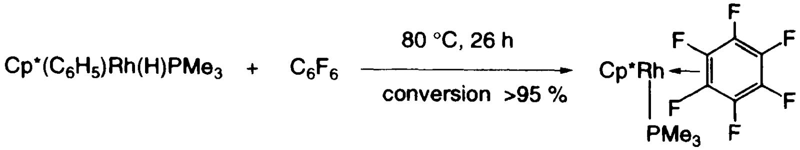


Figure 18.7 Structure of di-μ-chloro-dichlorobis(pentamethylchclopentadienyl)-dirhodium [43].

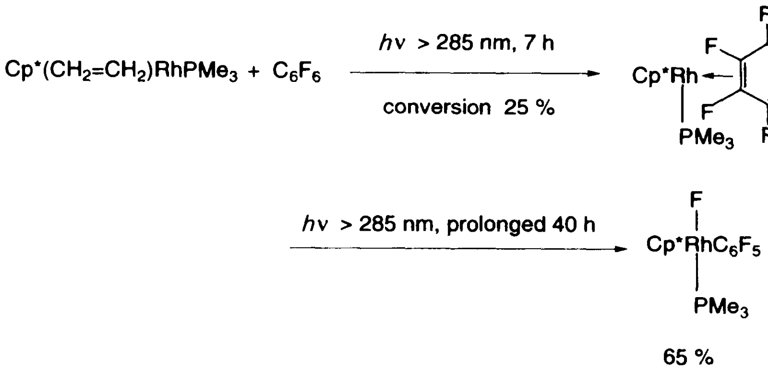
The reactions of organorhodium compounds or the catalytic reaction of a rhodium complex are insertions, formation reactions of carbene, hydrogenations, hydrometalations, decarbonylations, carbonylations, hydroformylations, cyclizations and cyclometalations, etc.

18.5.1 INSERTIONS

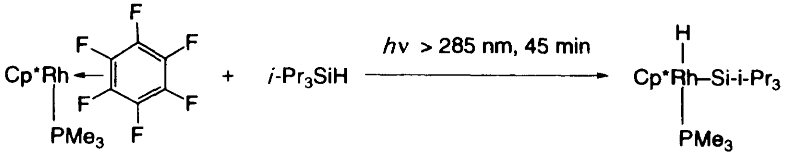
Pentamethylcyclopentadienylrhodium reacts with hexafluorobenzene to afford a hexafluorobenzene π-complex by both heating and light irradiation as shown in eqs. (18.23) and (18.24) [45]. The π-complex is stable in hexafluorobenzene to light for a short period (within 7h); however, in benzene or i-Pr_3SiH, it inserts into the C–H or Si–H bond to give $Cp^*Rh(PMe_3)(Ph)(H)$ or $Cp^*Rh(PMe_3)(H)(Si$-i-$Pr_3)$. An example of Si–H insertion is shown in eq. (18.25) [45]. $Cp^*Rh(PMe_3)(Ph)(H)$ which is the reaction product with benzene, reacts with fused ring polycyclic compounds such as naphthalene, anthracene and phenanthrene to afford the η^2-complex as shown in eqs. (18.23) and (18.24). However, with heating with naphthalane in an ampoule, both the CH insertion product and η^2-complex are yielded as shown in eq. (18.26) [46].



(18.23)



(18.24)



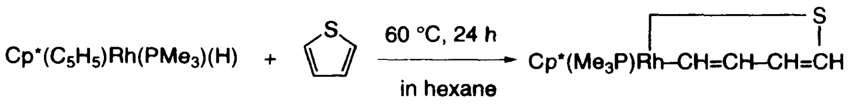
(18.25)

$$\mathrm{Cp^*(C_6H_5)Rh(PMe_3)(H)} \quad + \quad \mathrm{C_{10}H_8} \xrightarrow[\text{in hexane}]{60\ ^\circ\mathrm{C},\ 24\ \mathrm{h}\ ,\ \text{in glass ampoule}}$$

$$\mathrm{Cp^*(\eta^1\text{-}C_{10}H_7)Rh(PMe_3)(H)} \quad + \quad \mathrm{Cp^*(\eta^2\text{-}C_{10}H_8)Rh(PMe_3)} \qquad (18.26)$$

1 : 2 yield 100

In the reaction with sulfur compounds such as thiophenes, S–C insertion proceeds as shown in eq. (18.27) [47–49].

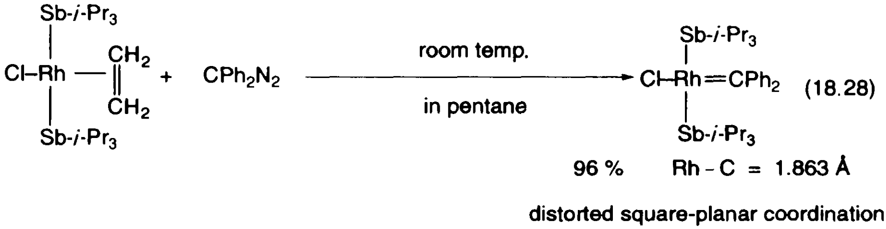


93 % (18.27)

18.5.2 FORMATION REACTIONS OF CARBENES

In organorhodium compounds, reaction with diazomethane [50–52], and rearrangement with acetylene compounds, etc. [53–62], afford a variety of carbene complexes. The carbenes are a general term for a chargeless divalent carbon (X(Y)C:) and the triplet state bond angle is ca. 150°) is more stable by ca. 10kcal/mol than the singlet state (bond angle ca. 100°). The metal complexes of a carbene are represented as M=CRR′ and when R and R′ are C or H, it is called an alkylidene complex. The carbene is labile, but the carbene complexes are relatively stable.

Rhodium compounds easily react with diazomethane to afford the carbene complex as shown in eq. (18.28) [50–52].



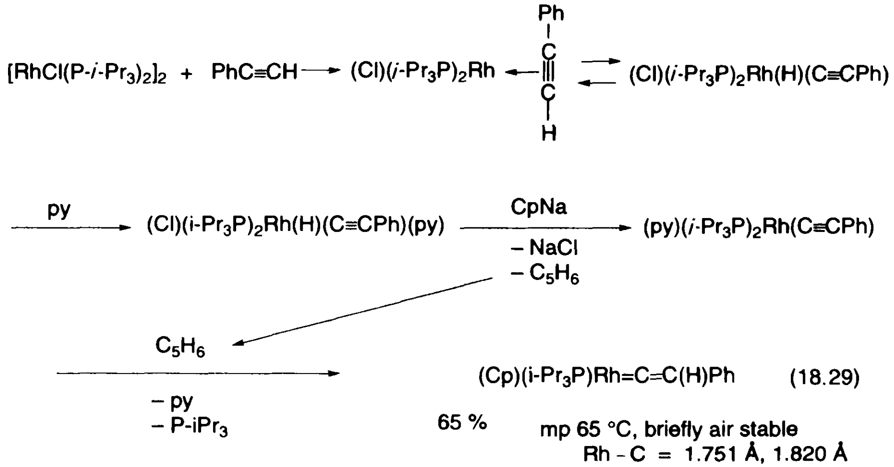
(18.28)

96 % Rh - C = 1.863 Å

distorted square-planar coordination

As shown in eq. (18.29), coordination-unsaturated rhodium compounds react with acetylene, and a π-coordination and σ-coordination come to an equilibrium. Then by adding pyridine the equilibrium is favorable to the σ-coordination. Then CpNa adds to produce the carbene complex [53].

As shown in eqs. (18.30) and (18.31), the heating and light irradiation of the rhodium–acetylene π-complex also afford the carbene complexes [56,62].

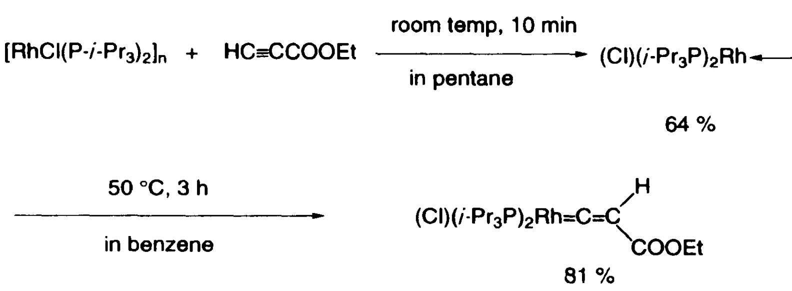


(18.29)

65 % mp 65 °C, briefly air stable

Rh - C = 1.751 Å, 1.820 Å

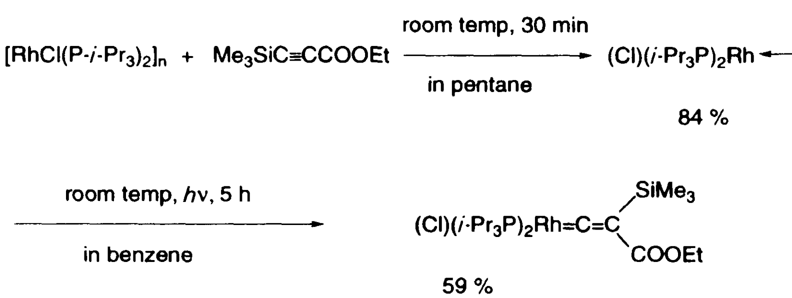
one unit of two molecules



$$[RhCl(P\text{-}i\text{-}Pr_3)_2]_n + HC{\equiv}CCOOEt \xrightarrow[\text{in pentane}]{\text{room temp, 10 min}} (Cl)(i\text{-}Pr_3P)_2Rh \leftarrow \overset{\displaystyle H}{\underset{\displaystyle COOEt}{C{\equiv}C}} \quad 64\,\%$$

$$\xrightarrow[\text{in benzene}]{50\,^{\circ}C,\ 3\ h} (Cl)(i\text{-}Pr_3P)_2Rh{=}C{=}C\begin{matrix}H\\COOEt\end{matrix} \quad 81\,\%$$

(18.30)



$$[RhCl(P\text{-}i\text{-}Pr_3)_2]_n + Me_3SiC{\equiv}CCOOEt \xrightarrow[\text{in pentane}]{\text{room temp, 30 min}} (Cl)(i\text{-}Pr_3P)_2Rh \leftarrow \overset{\displaystyle SiMe_3}{\underset{\displaystyle COOEt}{C{\equiv}C}} \quad 84\,\%$$

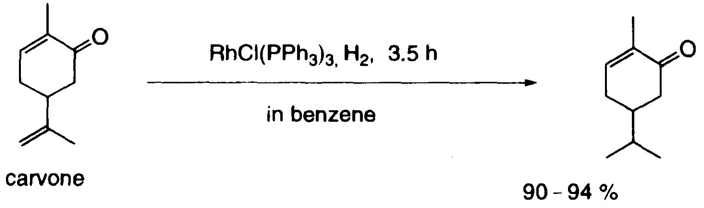
$$\xrightarrow[\text{in benzene}]{\text{room temp, } h\nu\text{, 5 h}} (Cl)(i\text{-}Pr_3P)_2Rh{=}C{=}C\begin{matrix}SiMe_3\\COOEt\end{matrix} \quad 59\,\%$$

(18.31)

18.5.3 HYDROGENATIONS

Rhodium is used in a variety of catalysts. In particular, the Wilkinson complex $RhCl(PPh_3)_3$ as a rhodium catalyst is well known, and hydrogenations, hydrometalations, carbonylations, decarbonylations, isomerizations and cyclizations proceed selectively [34,63].

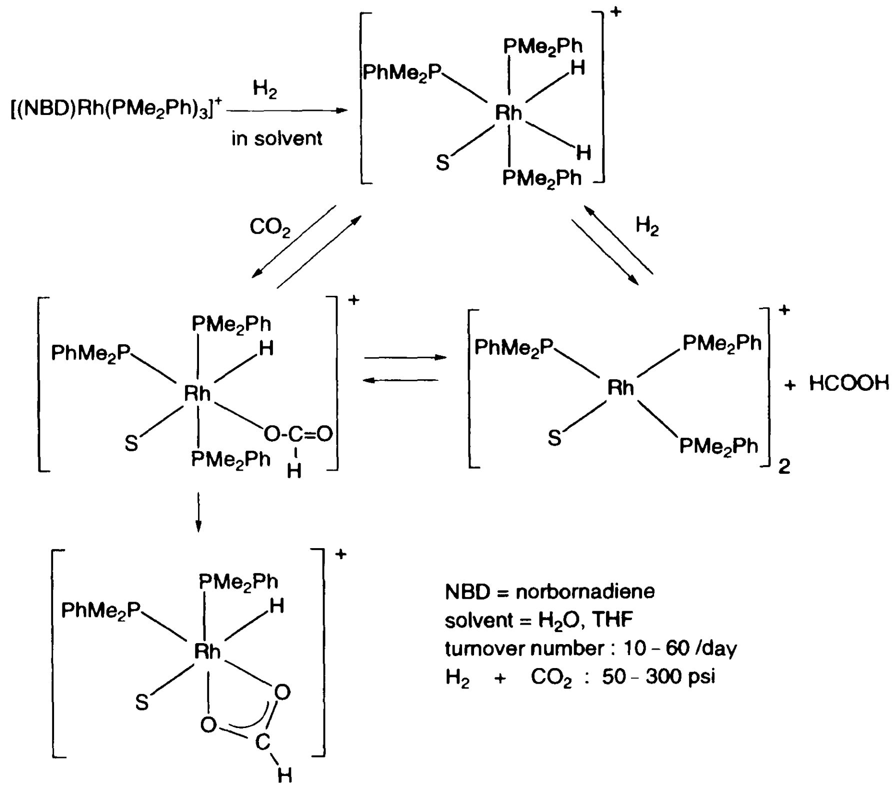
Besides the Wilkinson complex, $[(diene)RhCl]_2$ (diene = 1,5-cyclooctadiene, norbornadiene, etc.), $[Rh(P\text{-}P)(diene)]^+X^-$ ($X = BF_4$, ClO_4^-, PF_6, P-P = bisphosphine) and $Rh_6(CO)_{16}$ of a cluster complex, are used as rhodium catalysts [64]. The selective hydrogenation of an olefin with a Wilkinson complex is shown in eq. (18.32). The carvone absorbed hydrogen readily and quantitatively to afford dihydrocarvone in high yield [64].



carvone

90 - 94 %

(18.32)

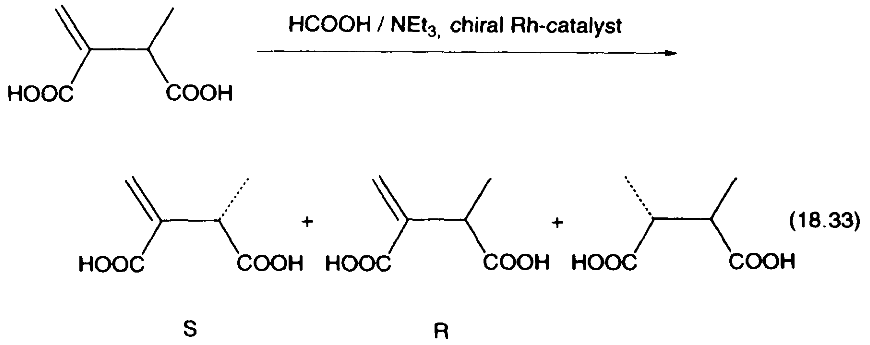


NBD = norbornadiene
solvent = H_2O, THF
turnover number : 10 - 60 /day
H_2 + CO_2 : 50 - 300 psi

Scheme 18.2 [65]

As shown in Scheme 18.2, with $[(NBD)Rh(PMe_2Ph)_3]BF_4$ as catalysts, the hydrogenation of carbon dioxide affords formic acid. The rhodium is coordinated with two hydrogen and one oxygen atom of water or tetrahydrofuran as solvent and the complex is thought to be an active catalyst. The monodentate or bidentate ligand of formic acid is confirmed by IR and NMR [65]. When $[Rh(COD)(\mu\text{-}H)]_4$ and $Ph_2P(CH_2)_4PPh_2$ are used as the catalyst, the reaction is very fast, and formic acid is obtained by 2200 moles to one mole of rhodium catalyst [66].

Hydrogenation with a chiral rhodium complex as catalyst affords stereoselective products as shown in eq. (18.33). When the racemate of the raw material is hydrogenated in 54% conversion, the R isomer, which is less reactive, is obtained in 84% purity, and when the racemate is hydrogenated in 70% conversion, pure R isomer is obtained. $HCOOH/NEt_3$ is used as the hydrogen source. The reaction shown in eq. (18.33) is the reverse reaction of that shown in Scheme 18.2 which is the hydrogenation of carbon dioxide [67].



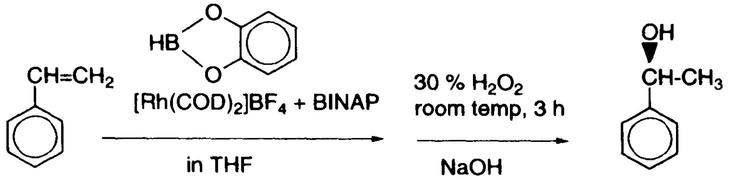
(18.33)

catalyst : [Rh(NBD)Cl]$_2$ + (2S,4S)-1-(t-butoxycarbonyl)-4-(diphenylphosphino)-2-(dipheyl-phosphino)methyl)pyrrolidine

As the asymmetric hydrogenations of amino acid with various kinds of chiral phosphinerhodium complexes as catalysts [68–70], the selective hydrogenations of heteroaromatic compounds [71] have been also reported.

18.5.4 HYDROMETALATIONS

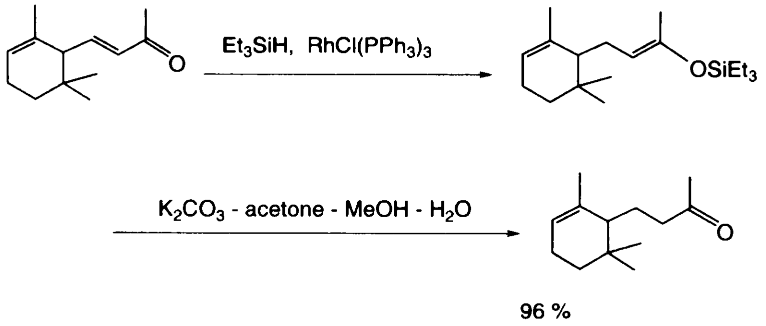
The examples of hydrometalations are hydroboration [64,72–77], hydrosilylation [78], etc. [78,79] of unsaturated compounds such as olefins, acetylenes, carbonyls and imines. For example, styrene reacts with catecholboran in the presence of a rhodium catalyst to afford stereoselectively the R isomer of 2-phenylethanol as shown in eq. (18.34) [72].



(18.34)

BINAP = (+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl

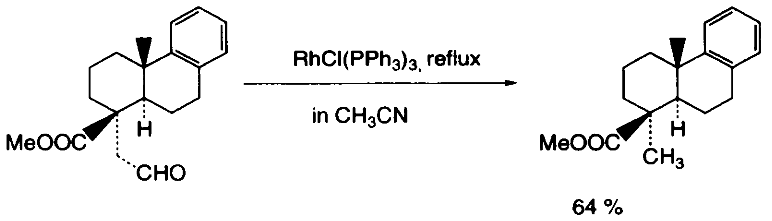
The hydrosilylation of ketone is shown in eq. (18.35). The selective hydrogenation reaction almost quantitatively proceeds under mild reaction conditions.



(18.35)

18.5.5 DECARBONYLATIONS

The Wilkinson complex $RhCl(PPh_3)_3$ is a coordination unsaturated compound as shown in eqs. (18.19) and (18.20). Since it has three bulky triphenylphosphine, it is able to react with a large molecule of hexafluorobutadiene via releasing one triphenylphosphine. But it is able to react directly with a small molecule of hydrogen or carbonyl. Hence, with the Wilkinson complex or similar catalysts having bulky ligands, their hydrogenations, decarbonylations and carbonylations proceed stereoselectively. As decarbonylation is the reaction that the carbonyl of aldehydes or acid halides bonds with rhodium atom, the reaction proceeds stoichiometrically with a high stereoselective retention [63,64,70,80,81]. For example, as shown in eq. (18.36), a decarbonylation product with a stereoselective retention is obtained by treatment of an aldehyde with a Wilkinson complex.



(18.36)

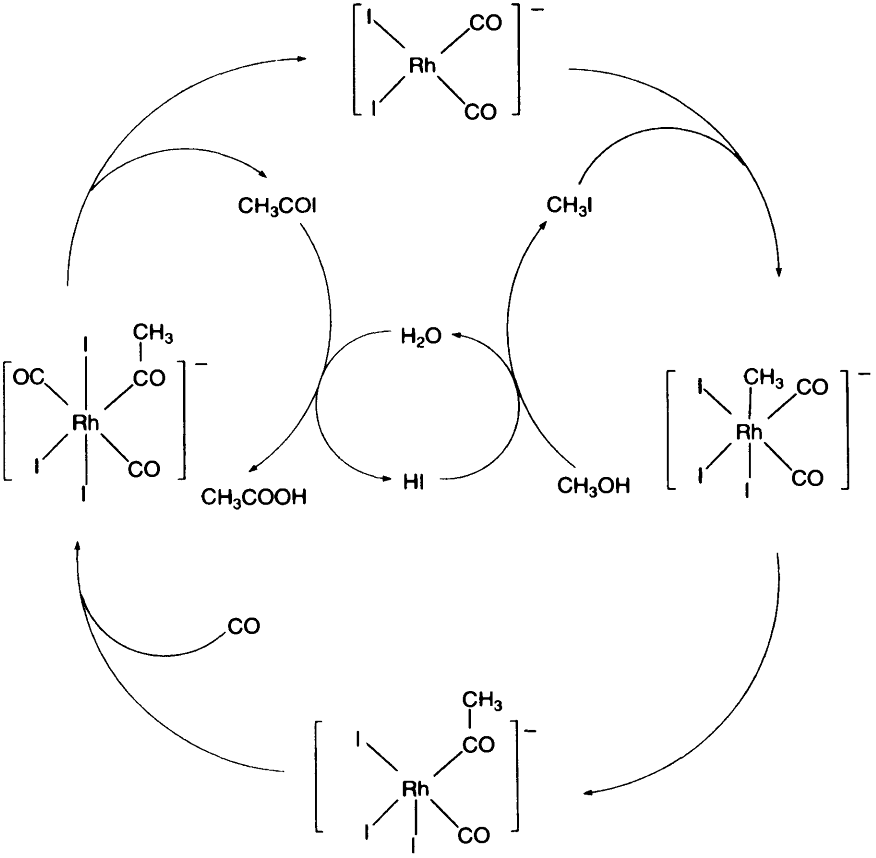
18.5.6 CARBONYLATIONS

The representative carbonylations with rhodium catalysts is the Monsanto acetic acid process which started in 1970 with a production amount of three million pounds per year [82–91]. In this carbonylation, the oxo process of the Reppe reaction is carried out at 250–270 °C, 200–300 atm with nickel catalysts, and the BASF process is carried out at 210 °C, 530 atm with a Co/I catalyst. However, the Monsanto acetic acid process shown in eq. (18.37) is carried out under mild reaction conditions in a high selectivity of acetic acid with rhodium catalyst. The catalyst is $RhCl_3 \cdot 3H_2O$ and the active species is considered to be $[Rh(CO)_2I_2]^-$

bonded with iodine and carbonyl. The reaction mechanism is shown in Scheme 18.3 [86,87]. At first, CH_3I, obtained by reaction of methanol and HI, is oxidatively added to the rhodium atom, with methyl migration and reductive elimination to afford acetic acid. The structure of the intermediate $[(CH_3CO)Rh(CO)_2I_3]^-$, obtained by the reaction of $[Rh(CO)(CH_3CO)I_3]$ with CO, is determined by X-ray diffraction studies [84,91].

$$CH_3OH \quad + \quad CO \xrightarrow{\text{Rh cat., HI, 180 °C, 30 - 40 atm}} \underset{99\ \%}{CH_3COOH} \qquad (18.37)$$

Rh cat. = $RhCl_3 \cdot 3H_2O$, $[RhCl(CO)_2]_2$, $Rh(PPh_3)_2(CO)Cl$, etc.

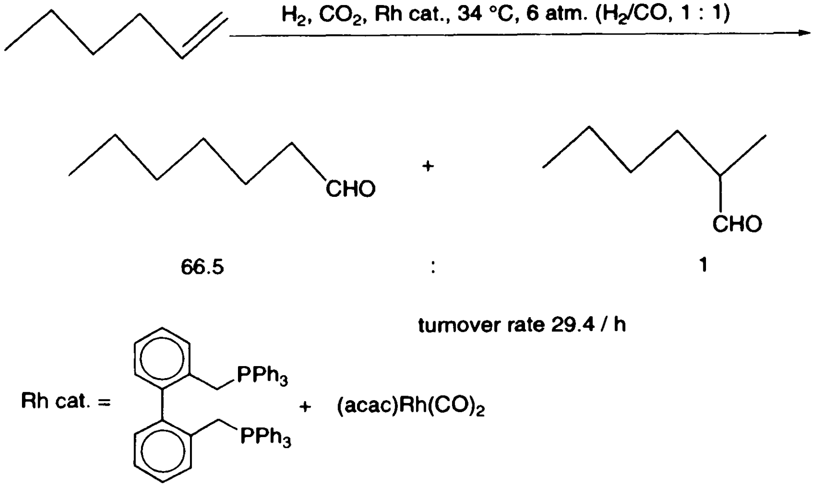


Scheme 18.3 Cycle for the rhodium and iodine catalyzed carbonylation of methanol to acetic acid [86].

The Monsanto acetic acid process is not only used for the carbonylation of methanol, but also for the carbonylation of ethanol, propanol, ethylene and propene to afford C3–C4 monocarboxylic acid, and a similar mechanism to that shown in Scheme 18.3 is thought to occur for these reactions [92].

18.5.7 HYDROFORMYLATIONS

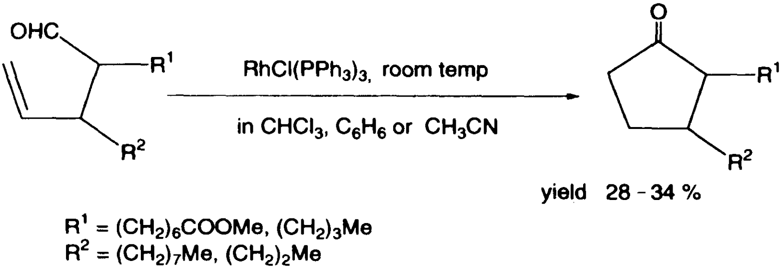
Hydroformylation is the reaction when hydrogenation and carbonylation proceed at the same time [93–97a]. The reaction of an olefin, hydrogen and carbonyl at high temperature and high pressure is not highly selective. But the mild reaction conditions with rhodium catalysts improves the reaction selectivity [93]. For example, as shown in eq. (18.38), when 1-hexene reacts, the ratio of 1-heptanol to 2-heptanol is 66.5 [96]. If the reaction is conducted using a highly optical pure phosphine rhodium catalyst, the aldehyde is obtained in a high ee% yield [94].



(18.38)

18.5.8 CYCLIZATIONS

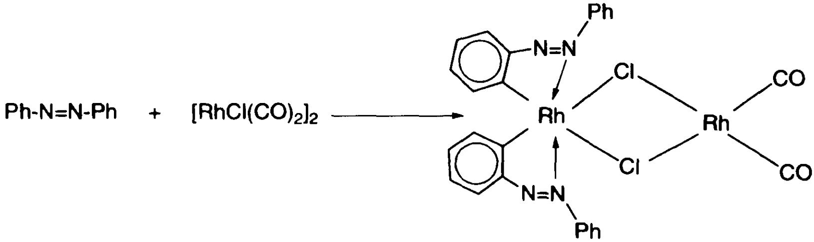
In the coordination unsaturated compounds (which are able to coordinate with one or two ligands) such as the Wilkinson complex, an aldehyde carbonyl, nitrogen group of diazo compound and carbon–carbon unsaturated bond oxidatively add to the compounds, and the cyclization is liable to proceed by reductive elimination [98–102]. For example, 4-pentene-1-al derivative reacts in the presence of the Wilkinson complex to afford prostaglandin derivatives by cyclization [98,101]. When the reaction is performed with a chiral rhodium complex, the cyclization product is obtained in a high ee% yield [102]. The cyclization usually forms five or six-membered ring compounds, the reaction of a diazo compound with acetylenic compounds or with olefin forming cyclopropene or cyclopropane compounds of three-membered rings [100].



(18.39)

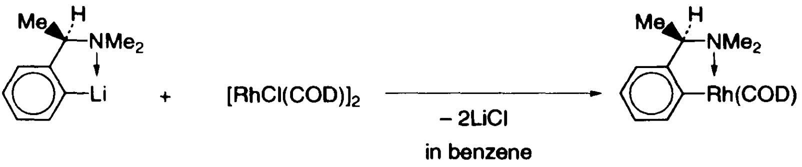
18.5.9 CYCLOMETALATIONS

The cyclometalations of azobenzenes, benzyldeneanilines, benzo[*h*]quinoline, benzene-ketoximes, and acetophenone with rhodium compounds have been reported [103–109c]. Examples of azobenzene are shown in eq. (18.40). These products are



(18.40)

mostly five-membered ring compounds. If the reaction of cyclometalations is low, these cyclization compounds are prepared by a transmetalation. An example of transmetalation is shown in eq. (18.41) [110,111].



(18.41)

18.5.10 OTHERS

The other reactions with rhodium compounds are oxidation [63], additions [63,112,113], isomerizations [70,114–116], dehydrogenations [117], hydrogenolyses [118], hydroaluminations [119], hydroacetylations [120], dimerizations [121–123] and polymerization.

Polyacetylene is expected to be an electroconductive polymer. Polymerization with organorhodium compounds easily affords a highly stereoselective polymer. For example, the polymerization of phenylacetylene with $[(NBD)RhCl]_2$ in a triethylamine solvent affords a polymer having a cis-transoid structure with mol. wt. 520000 in 93% yield [124,125].

REFERENCES

[1] *Kagaku Daijiten*, Tokyo Kagaku Doojin, Tokyo, p. 2557, 1989. H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
[2] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., John Wiley, New York, vol.18, p. 228, 1980.
[3] *The Merck Index 11th ed.*, 1989.
[4] *Sekai Dai Hyakkajiten*, Heibonsha, Tokyo, vol. 30, p. 374, 1988.
[5] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, 4th ed., p. 1409, 1987.
[6] *Sekai Kagaku Daijiten, Technopia (Encyclopedia of Science and Technology)*, Kodansha, Tokyo, vol.18, p. 400, 1977.
[7] *Jikken Kagaku Kouza 18, 4th ed., Yuki Kinzoku Sakutai*, Japan Chem. Soc. ed., Maruzen, Tokyo, p. 327, 1991.
[8] I. Yamamoto ed., *Yuki Kinzoku Kagoubutsu, Goseiho oyobi Riyouhou*, Tokyo Kagaku Dojin, Tokyo, p. 200, 1991.
[9] P.E. Cattermole and A.G. Osbore, *Inorganic Synthesis*, **17** (1977) 115.
[10] P. Chini and S. Martinengo, *J. Chem. Soc. Commun.*, (1968) 251.
[11] S.H.H. Chaston and F.G.A. Stone, *J. Chem. Soc. A*, (1969) 500.
[12] S. Martinengo, G. Giordano and P. Chini, *Inorganic Synthesis*, **20** (1980) 209.
[13] P.E. Cattermole and A.G. Osborne, *J. Organomet. Chem.*, **37** (1972) C17.
[14] B.R. James, G.L. Rempel and W.K. Teo, *Inorganic Synthesis*, **16** (1976) 49.
[15] B.L. Booth, M.J. Else, R. Fields, H. Goldwhite and R.N. Haszeldine, *J. Organomet. Chem.*, **14** (1968) 417.
[16] J.A. McCleverty and G. Wilkinson, *Inorganic Synthesis*, **8** (1966) 211.
[17] D. Evans, J.A. Osborn and F. Wilkinson, *Inorganic Synthesis*, **11** (1968) 99.
[18] D. Evans. G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, (1968) 2660.
[19] J. Powell and B.L. Shaw, *J. Chem. Soc. A*, (1968) 583.
[20] R.P. Hughes, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G. A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.5, p. 278, 1982.
[21] R. Cramer, *Inorganic Synthesis*, **15** (1977) 14.
[22] R. Cramer, *Inorg. Chem.*, **1** (1962) 722.
[23] R.B. King, *Inorg. Chem.*, **2** (1963) 528.
[24] J. Chatt and L.M. Venanzi, *J. Chem. Soc.*, (1957) 4735.
[25] R.B. King, *Organometallic Synthesis*, vol.1, p. 132, Academic Press, New York, 1965.
[26] Y. Ishii, H. Hoshi, Y. Hamada and M. Hidai, *Chem. Lett.*, (1994) 801.
[27] J.W. Kang, K. Moseley and P.M. Maitlis, *J. Am. Chem. Soc.*, **91** (1969) 5970.
[28] B.L. Booth, R.N. Haszeldine and M. Hill, *J. Chem. Soc. A*, (1969) 1299.
[29] Y. Wakatsuki and H. Yamazaki, *J. Organomet. Chem.*, **64** (1974) 393.
[30] G. Hogarth, M. Arthurs, J.C. Bickerton, L. Daly, C. Piper, D. Ralfe and D.A. Morton-Blake, *J. Organomet. Chem.*, **467** (1994) 145.

[31] M. Arthurs, J. Bickerton, G. Kubal, J. O'Sullivan, C. Piper, G. Hogarth and D.A. Morton-Blake, *J. Organomet. Chem.*, **467** (1994) 135.

[32] M. Arthurs, S.M. Nelson and M.G.B. Drew, *J. Chem. Soc. Dalton Trans.*, (1977) 779.

[33] R. Blom, D.W.H. Rankin, H.E. Robertson and R.N. Perutz, *J. Chem. Soc. Dalton Trans.*, (1993) 1983.

[34] F.H.Jardine, *Prog. Inorg. Chem.*, **28** (1981) 63.

[35] R.P. Hughes, P.R. Rose and A.L. Rheingold, *Organometallics*, **12** (1993) 3109.

[36] O.V. Gusev, S. Sergeev, I.M. Saez and P.M. Maitlis *Organometallics*, **13** (1994) 2059.

[37] M. Bortolin, U.E. Bucher, H. Rüegger, L.M. Venanzi, A. Albinati, F. Lianza and S. Trofimenko, *Organometallics*, **11** (1992) 2514.

[38] H.L.M. van Gaal, F.G. Moers and J.J. Steggerda, *J. Organomet. Chem.*, **65** (1974) C43.

[39] C. Busetto, A. D'Alfonso, F. Maspero. G. Perego and A. Zazzetta, *J. Chem. Soc. Dalton Trans.*, (1977)1828.

[40] C.H. Wei, G.R. Wilkes and L.F. Dahl, *J. Am. Chem. Soc.*, **89** (1967) 4792.

[41] E.R. Corey, L.F. Dahl and W. Beck, *J. Am. Chem. Soc.*, **85** (1963) 1202.

[42] L.F. Dahl, C. Martell and D.L. Wampler, *J. Am. Chem. Soc.*, **83** (1961) 1761.

[43] M.R. Churchill, S.A. Julis and F.J. Rotella, *Inorg. Chem.*, **16** (1977) 1137.

[43a] J.E. Collins, M.P. Castellam, A.L. Rheingold, E.J. Miller, W.E. Geiger, A.L. Rieger and P.H. Rieger, *Organometallics*, **14** (1995) 1232.

[43b] H. Adams, N.A. Bailey, B.E. Mann, B.F. Taylor, C. White and P. Yavari, *J. Chem. Soc. Dalton Trans.*, (1987) 1947.

[44] J. Müller, H.-O. Stühler, W. Goll, *Chem. Ber.*, **108** (1975) 1074.

[45] S.T. Belt, M. Helliwell, W.D. Jones, M.G. Partridge and R.N. Perutz, *J. Am. Chem. Soc.*, **115** (1993) 1429.

[46] R.M. Chin, L. Dong, S.B. Duckett, M.G. Partridge, W.D. Jones and R.N. Perutz, *J. Am. Chem. Soc.*, **115** (1993) 7685.

[47] W.D. Jones and K. Dong, *J. Am. Chem. Soc.*, **113** (1991) 559.

[48] W.D. Jones and R.M. Chin, *J. Am. Chem. Soc.*, **114** (1992) 9851.

[49] S. Luo, A.E. Skaugset, T.B. Rauchfuss and S.R. Wilson, *J. Am. Chem. Soc.*, **114** (1992) 1732.

[50] P. Schwab, N. Mahr, J. Wolf and H. Werner, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 1480.

[51] H. Werner, *J. Organomet. Chem.*, **475** (1994) 45.

[52] H. Werner and U. Möhring, *J. Organomet. Chem.*, **475** (1994) 277.

[53] J. Wolf, H. Werner, O. Serhadli and M.L. Ziegler, *Angew, Chem. Int. Ed. Engl.*, **22** (1983) 414.

[54] F.J. G. Alonso, A. Höhn, J. Wolf, H. Otto and H. Werner, *Angew. Chem. Int. Ed. Engl.*, **24** (1985) 406.

[55] M.I. Bruce, *Chem. Rev.*, **91** (1991) 197.

[56] H. Werner, J. Wolf, F.J.G. Alonso, M.L. Ziegler and O. Serhadli, *J. Organomet. Chem.*, **336** (1987) 397.

[57] M. Schäfer, J. Wolf and H. Werner, *J. Chem. Soc. Commun.*, (1991) 1341.

[58] H. Werner, D. Schneider and M. Schulz, *J. Organomet. Chem.*, **451** (1993) 175.

[59] R. Wiedermann, P. Steinert, M. Schäfer and H. Werner, *J. Am. Chem. Soc.*, **115** (1993) 9864.

[60] H. Werner, M. Baum, D. Schneider and B. Windmüller, *Organometallics*, **13** (1994) 1089.

[61] H. Werner, T. Rapport. R. Wiedemann, J. Wolf and N. Mahr, *Organometallics*, **13** (1994) 2721.

[62] D. Schneider and H. Werner, *Angew. Chem. Int. Ed. Engl.*, **30** (1991) 700.

[63] J. Tsuji, *Kagaku*, **27** (1972) 292,382.
[64] *Jikken Kagaku Kouza 25, 4th ed., Yuki Gosei, VII, Yuki Kinzoku, Shiyaku niyoru Gosei*, Japan Chem. Soc. ed., Maruzen, Tokyo, p. 349, 1991.
[65] J.-C. Tsai and K.M. Nicholas, *J. Am. Chem. Soc.*, **114** (1992) 5117.
[66] W. Leitner, E. Dinjus and F. Gassner, *J. Organomet. Chem.*, **475** (1994) 257.
[67] W. Leitner, J.M. Brown and H. Brunner, *J. Am. Chem. Soc.*, **115** (1993) 152.
[68] W.S. Knowles, *Acc. Chem. Res.*, **16** (1983) 106.
[69] U. Nagel and T. Krink, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 1052.
[70] I. Ojima, *Kagaku Zokan*, **96** (1982) 85.
[71] E. Baralt, S.J. Smith, J. Hurwitz, I.T. Horváth and R.H. Fish, *J. Am. Chem. Soc.*, **114** (1992) 5187.
[72] T. Hayashi, Y. Matsumoto and Y. Ito, *J. Am. Chem. Soc.*, **111** (1989) 3426.
[73] K. Burgess, W.A. van der Donk, M. B. Jarstfer and M.J. Ohlmeyer, *J. Am. Chem. Soc.*, **113** (1991) 6139.
[74] D.A. Evans, G.C. Fu and A.H. Hoveyda, *J. Am. Chem. Soc.*, **114** (1992) 6671.
[75] D.A. Evans, G.C. Fu and B.A. Anderson, *J. Am. Chem. Soc.*, **114** (1992) 6679.
[76] S.A. Westcott, H.P. Blom, T.B. Marder and R.T. Baker, *J. Am. Chem. Soc.*, **114** (1992) 8863.
[77] H.C. Brown, *Hydroboration*, Wiley-Interscience, New York, 1962.
[78] I. Oijima, T. Kogure and Y. Nagai, *Tetrahedron Lett.*, (1972) 5035.
[79] I. Ojima, T. Kogure, M. Nihonyanagi and Y. Nagai, *J. Org. Chem.*, **45** (1980) 3506.
[80] B.M. Trost, and M. Preckel, *J. Am. Chem. Soc.*, **95** (1973) 7862.
[81] H.M. Walborsky and L.E. Allen, *J. Am. Chem. Soc.*, **93** (1971) 5465.
[82] F.E. Paulik and J.F. Roth, *J. Chem. Soc. Commun.*, (1968) 1578.
[83] J.F. Roth, J.H. Craddock, A. Hershman and F.E. Paulik, *Chem. Tech*, Oct. (1971)600.
[84] D. Forster, *Adv. Organomet. Chem.*, **17** (1979) 255.
[85] J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Application of Organotransition Metal Chemistry*, University Science Books, California, p. 638, 1987.
[86] A. Haynes, B.E. Mann, D.J. Gulliver, G.E. Morris and P.M. Maitlis, *J. Am. Chem. Soc.*, **113** (1991) 8567.
[87] A. Haynes, B.E. Mann, G.E. Morris and P.M. Maitlis, *J. Am. Chem. Soc.*, **115** (1993) 4093.
[88] D. Forster and T.W. Dekleva, *J. Chem. Educ.*, **63** (1986) 204.
[89] G.W. Parshall (translator A. Miyashita), *Kagaku Zokan*, **105** (1985) 151.
[90] G.W. Parshall, *Science*, **208** (1980) 1221.
[91] G.W. Adamson, J.J. Daly and D. Forster, *J. Organomet, Chem.*, **71** (1974) C17.
[92] D.C. Roe, R.E. Sheridan, E.E. Bunel, *J. Am. Chem. Soc.*, **116** (1994) 1163.
[93] G.D. Cuny and S.L. Buchwald, *J. Am. Chem. Soc.*, **115** (1993) 2066.
[94] N. Sakai, S. Mano, K. Nozaki and H. Takaya, *J. Am. Chem. Soc.*, **115** (1993) 7033.
[95] L. Kollár and P. Sándor, *J. Organomet. Chem.*, **445** (1993) 257.
[96] C.P. Casey, G.T. Whiteker, M.G. Melville, L.M. Petrovich, J.A. Gavney, Jr. and D.R. Powell, *J. Am. Chem. Soc.*, **114** (1992) 5535.
[97] G. Süss-Fink, *Angew. Chem. Int. Ed. Engl.*, **33** (1994) 67.
[97a] H. Takaya, N. Sakai and K. Nozaki, *Shokubai*, **36** (1994) 259.
[98] K. Sakai, *Yuki Gosei Kagaku Kyokaishi*, **51** (1993) 733.
[99] A. Padwa, D.J. Austin, S.F. Hornbuckle and M.A. Semones, *J. Am. Chem. Soc.*, **114** (1992) 1874.
[100] M.N. Protopopova, M.P. Doyle, P. Müller and D. Ene, *J. Am. Chem. Soc.*, **114** (1992) 2755.
[101] K. Sakai, J. Ide, O. Oda and N. Nakamura, *Tetrahedron Lett.*, (1972) 1287.
[102] X.-M. Wu, K. Funakoshi and K. Sakai, *Tetrahedron Lett.*, **33** (1992) 6331.

[102a] I. Matsuda, *Yuki Gosei Kagaku Kyokaishi*, **52** (1994) 800.

[103] I. Omae, *Organometallic Intramolecular-coordination Compounds, J. Organometallic Chemistry Library 18*, Elsevier, Amsterdam, 1986.

[104] M.I. Bruce, B.L. Goodall, M.Z. Iqbal and F.G.A. Stone, *J. Chem. Soc. Commun.*, (1971) 661.

[105] M.I. Bruce, B.L. Goodall and F.G.A. Stone, *J. Organomet. Chem.*, **60** (1973) 343.

[106] O. Nürnberg and H. Werner, *J. Organomet. Chem.*, **460** (1993) 163.

[107] M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, *J. Organomet. Chem.*, **40** (1972) 393.

[108] A.R. Garber, P.E. Garrou, G.E. Hartwell, M.J. Smas, J.R. Wilkinson and L.J. Todd, *J. Organomet, Chem.*, **86** (1975) 219.

[109] H. Onoue and I. Moritani, *J. Organomet. Chem.*, **44** (1972) 189.

[109a] W.C. Kaska, S. Nemeh, A. Shirazi and S. Potuznik, *Organometallics*, **7** (1988) 13.

[109b] A.A.H. van der Zeijden, G. van Koten, J.M. Ernsting, C.J. Elsevier, B. Krijnen and C.H. Stam, *J. Chem. Soc. Dalton Trans.*, (1989) 317.

[109c] J.W. Suggs and C.-H. Jun, *J. Am. Chem. Soc.*, **108** (1986) 4679.

[110] I.C.M. Wehman-Ooyevaar, J.A. Vedral, J.T.B.H. Jastrzebski, D.M. Grove and G. van Koten, *J. Organomet. Chem.*, **451** (1993) 195.

[111] I.C.M. Wehman-Ooyevaar, G.M. Kapteijin, D.M. Grove, W.J.J. Smeets, A.L. Spec and G. van Koten, *J. Chem. Soc. Dalton Trans.*, (1994) 703.

[112] M. Sawamura, H. Hamashima and Y. Ito, *J. Am. Chem. Soc.*, **114** (1992) 8295.

[113] C. Mercier and P. Chabardes, *Pure Appl. Chem.*, **66** (1994) 1509.

[114] H. Nishiyama, *Kagaku Sousetsu*, **19** (1993) 91.

[115] K. Tani, *Kagaku Zokan*, **105** (1985) 121.

[116] L. Cassar, P.E. Eaton and J. Halpern, *J. Am. Chem. Soc.*, **92** (1970) 3515.

[117] J.A. Maguire, A. Petrillo and A.S. Goldman, *J. Am. Chem. Soc.*, **114** (1992) 9492.

[118] C. Perthuisot and W.D. Jones, *J. Am. Chem. Soc.*, **116** (1994) 3647.

[119] J.-J. Brunet, G. Commenges, D. Neibecker and K. Philippot, *J. Organomet. Chem.*, **469** (1994) 221.

[120] R.W. Barnhart, X Wang, P. Noheda, S.H. Bergens, J. Whelan and B. Bosnich, *J. Am. Chem. Soc.*, **116** (1994) 1821.

[121] M. Brookhart and S. Sabo-Etienne, *J. Am. Chem. Soc.*, **113** (1991) 2777.

[122] M. Brookhart and E. Hauptman, *J. Am. Chem. Soc.*, **114** (1992) 4437.

[123] M. Schäfer, N. Mahr, J. Wolf and H. Werner, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 1315.

[124] M. Tabata and K. Yokota, *Kagaku Kogyo*, **44** (1993) 738.

[125] M. Tabata, *Kobunshi*, **44** (1995) 446.

19 Organonickel Compounds

19.1 INTRODUCTION

An organonickel compound, that is, nickel tetracarbonyl, discovered by Mond in 1890, is well known. This discovery was carried out by the cautious investigation of a trivial matter. This was an important discovery to show that we should investigate by taking even a slightly unusual occurrence seriously. By the investigation of the properties of this compound, the refinement process for high purity nickel was discovered. Then this refining process was applied to the production of other high purity metals such as iron and cobalt.

Almost 60–70% of chemicals are produced by catalytic reactions, and 10–15% of the catalysts in catalytic reactions are homogeneous catalysts. Among the homogeneous catalysts, cobalt catalysts are mainly used for hydroformylation reactions, and next to cobalt, nickel catalysts are used for many others. The organonickel compounds are used not only as catalysts in industrial production but also for organic synthesis in laboratories.

19.2 NICKEL

Nickel is a transition metal of group 10 in the periodic table, of which the outer shell electrons (valence electrons) are $3d^84s^2$. There is 80 ppm of nickel present in the Earth's crust. Elements with similar amounts in the Earth's crust are chromium (100 ppm), zinc (70 ppm) and copper (50 ppm) [1]. Nickel is produced from mainly three kinds of ore: pentlandite ($(Ni,Fe)_9S_8$), garnierite ($(Ni,Mg)_6Si_4O_{10}(OH)_8$) and laterite ($(Fe,Ni)O(OH).nH_2O$). In the case of the representative pentlandite in sulfide ores, at first the concentrate is produced by the separation, e.g., flotation and magnetic separation, and it is smelted in the smelting furnace. Then, the sulfide mixture of metals such as nickel and copper as the matte, and the others such as SiO_2 and MgO as the slag, are separated using their specific gravities. The matte is charged into a horizontal-type converter and the molten matte with added silica is blown with air, which removes virtually all the remaining iron as a slag and most of the sulfur as sulfur dioxide and yields a sulfur-deficient copper–nickel matte. This matte is pulverized and the nickel and copper sulfides are isolated by flotation and the alloy is extracted magnetically and refined electrically. The final nickel metal thus obtained has a purity exceeding 99.9% [2,3]. The properties of nickel are

Table 19.1 Properties of nickel [3–7]

Property	Value
melting point, °C	1455
boiling point, °C	2730
crystal structure	face-centered cubic
density, 20 °C, g/cm^3	8.908
specific heat at 20 °C, KJ/(Kg,K)	0.44
linear coefficient of thermal expansion at 0–100 °C	13.3×10^{-6}
electrical resistivity at 20 °C, $\mu\Omega$·cm	6.9
hardness	
Mohs scale	3.8
Brinell hardness	85
thermal conductivity, Wm^{-1}K^{-1}	88.5
heat of fusion at melting point, J/g	302
heat of vaporization (T crict), J/g	6375
heat capacity at 0–100 °C, J/g, K	0.452
temperature coefficient of electrical resistivity, K^{-1}	6.8×10^{-3}

shown in Table 19.1 [3–7]. They resemble iron, cobalt and copper. The +2 oxidation state is the most important in nickel chemistry, although the +3 and +4 oxidation states are also known. Nickel(II) ions form complexes very readily and its maximum coordination number is six. The most unusual property of nickel is its ability to react directly and easily with carbon monoxide at 60 °C to form volatile nickel tetracarbonyl ($Ni(CO)_4$). This reaction is reversible, with the carbonyl compound decomposing into carbon monoxide and nickel at a higher temperature (180 °C) as shown in eq. (19.1). The reverse reaction is used for the vapormetallurgical refining of high purity nickel. Nickel has an excellent corrosion resistance to air, sea water, alkali and nonoxidizing acids such as sulfuric acid, hydrochloric acid, and organic acids. Therefore nickel is used as an electroplating metal. Nickel has poor resistance to strongly oxidizing acids like nitric acid. Nickel is resistant to corrosion by caustic soda, but in contrast it is attacked by aqueous ammonia solutions. Nickel is resistant to corrosion by chlorine, hydrogen chloride, fluorine and molten salts.

$$\mathrm{Ni} \quad + \quad 4\mathrm{CO} \quad \xrightleftharpoons[\text{180 °C}]{\text{60 °C, atmospheric pressure}} \quad \mathrm{Ni(CO)_4} \qquad (19.1)$$

mp -17.2 °C, bp 42.2 °C
notoriously poisonous
threshold limit 0.001 ppm
colorless, volatile liquid

Nickel absorbs hydrogen, especially when finely divided, and the amount of hydrogen absorption increases with increasing temperature. Nickel is widely used mainly as pure metal, in plating, and in alloys such as stainless steel, Parmalloy (magnetic materials), monel metal (corrosion-resistant materials) and nichrom wire (electrically heated wire) for construction, machinery, automotive industry, chemical industry, building construction, power industry, petroleum industry, aerospace, marine applications, coinage, eyeglass frames, music instruments and others [3–8].

19.3 SYNTHESES OF ORGANONICKEL COMPOUNDS

Nickel compounds are synthesized mainly by the following five reaction methods.

(1) Carbonylation
(2) Reactions with nickel carbonyl compounds
(3) Reactions with unsaturated compounds
(4) Reactions with unsaturated organonickel π-complexes
(5) Others

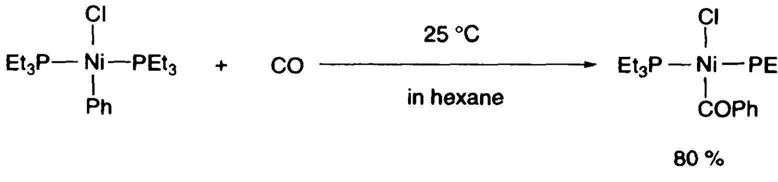
19.3.1 CARBONYLATION

As shown in eq. (19.1), nickel reacts with carbon monoxide under room temperature and atmospheric pressure. The pulverized nickel has a high reactivity and the rate of the reaction is dependent on its crystal form. $Ni(CO)_4$ is a highly volatile colorless liquid. It starts to decompose at 35 °C or higher and its boiling point is 42.2 °C. The toxicity is very high and the lethal dose is 0.001 ppm. The lethal dose of hydrocyanic acid gas and carbon monoxide are 10ppm and 100ppm, respectively. Hence the toxicity of $Ni(CO)_4$ is 10000 and 100000 times higher than these deadly poison gases [9,10].

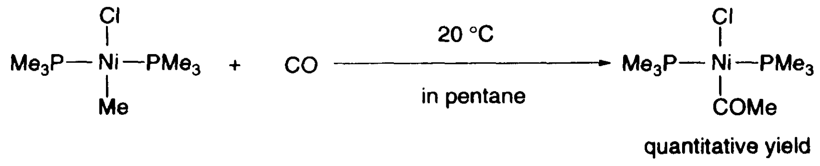
As shown in eqs. (19.2) and (19.3), the substitution reactions of nickel phosphines with carbon monoxide proceed easily [9]. But, in the reaction of phenylnickel compounds or methylnickel compounds with carbon monoxide, insertion reactions instead proceed as shown in eqs. (19.4) and (19.5) [11–15]. The X-ray diffraction data show that the acetyl nickel compounds as shown in eq. (19.5) has square planar geometry [13]. The carbonyl insertion reactions have been reported with various kinds of organic groups [9,16–19].

$$\mathrm{Ni(PMe_3)_4} \quad + \quad \mathrm{2CO} \longrightarrow \mathrm{Ni(CO)_2(PMe_3)_2} \quad + \quad \mathrm{2PMe_3} \qquad (19.2)$$

$$\mathrm{NiBr(PPh_3)_3} \quad + \quad \mathrm{2CO} \longrightarrow \mathrm{Ni(CO)_2(PPh_3)_2Br} \quad + \quad \mathrm{PPh_3} \qquad (19.3)$$



$$\mathrm{Et_3P{-}\underset{\displaystyle Ph}{\overset{\displaystyle Cl}{Ni}}{-}PEt_3} \quad + \quad \mathrm{CO} \xrightarrow[\text{in hexane}]{25\ ^{\circ}\mathrm{C}} \underset{80\ \%}{\mathrm{Et_3P{-}\underset{\displaystyle COPh}{\overset{\displaystyle Cl}{Ni}}{-}PEt_3}} \qquad (19.4)$$



$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{Me_3P{-}Ni{-}PMe_3}\\ |\\ \mathrm{Me}\end{array} + \mathrm{CO} \xrightarrow[\text{in pentane}]{20\ ^\circ\mathrm{C}} \begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{Me_3P{-}Ni{-}PMe_3}\\ |\\ \mathrm{COMe}\end{array} \quad (19.5)$$

quantitative yield

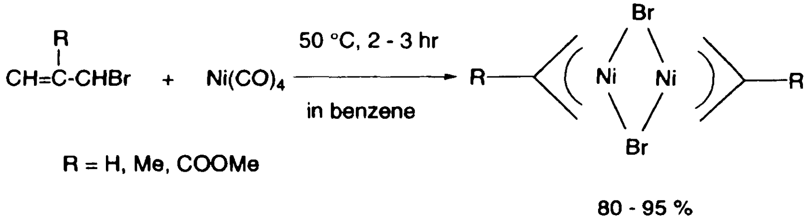
19.3.2 REACTIONS WITH NICKEL CARBONYL COMPOUNDS

Nickel tetracarbonyl ($Ni(CO)_4$) obtained by the reaction shown in eq. (19.1) is available as a starting material for the synthesis of organonickel compounds. For example, it reacts with a phosphine as shown in eq. (19.6). When the molar ratio of nickel tetracarbonyl and phosphine is 1 : 3, $Ni(CO)(PPh_3)_3)$ is produced, and $Ni(CO)_3(PPh_3)$ is produced in the molar ratio 1 : 1 of $Ni(CO)_4$ and PPh_3, or by the reaction of $NiBr_2(PPh_3)_2$ under a pressurized CO atmosphere (60 atm) [20].

$$\mathrm{Ni(CO)_4} + \mathrm{2PPh_3} \xrightarrow[\text{in ether}]{\text{reflux 30 min}} \mathrm{Ni(CO)_2(PPh_3)_2} + \mathrm{2CO} \quad (19.6)$$

mp 210 - 215 °C

Allyl bromide readily reacts with nickel tetracarbonyl to afford allylnickel bromide in high yield as shown in eq. (19.7) [21]. The allylnickel compound is available as allylation reagents. The reaction as shown in eq. (19.8) is one of the applications of allylnickel for synthesis of vitamin K_1 [22].

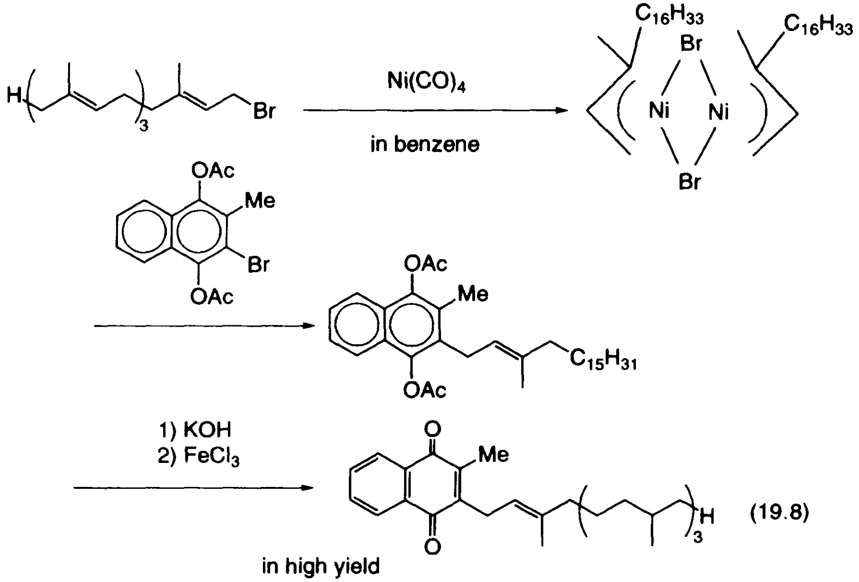


(19.7)

Nickel tetracarbonyl is a deadly poisonous volatile liquid as described above, and hence it is not so widely used as the starting material for the synthesis of organometallic compounds as $Fe(CO)_5$ and $Ru(CO)_{12}$.

19.3.3 REACTIONS WITH UNSATURATED COMPOUNDS

Unsaturated compounds such as monoolefins, dienes and acetylenes readily react with nickel halides or nickel acetylacetonates to afford their π-complexes. For example, the reactions shown in eqs. (19.9)–(19.12) give the π-complexes of an olefin, cyclodiene or cyclotriene [20,23–28].

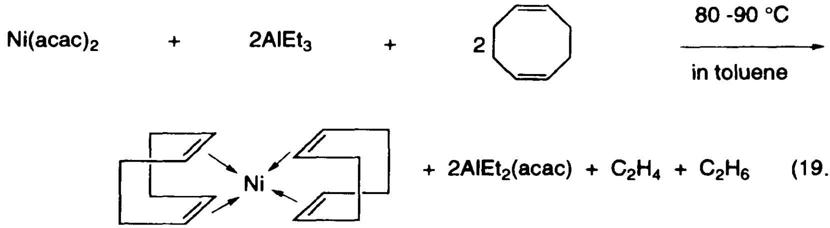


(19.8)

Vitamine K$_1$

$$Ni(acac)_2 + C_2H_4 + 2PPh_3 \xrightarrow{AlEt_3,\ 0\ °C,\ 24\ hr} (C_2H_4)Ni(PPh_3)_2 \quad (19.9)$$

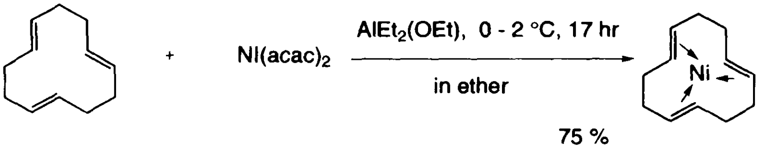
85 %



(19.10)

(COD)$_2$Ni 60 %

decomp. ca. 135 - 140 °C
sol. in benzene, THF, etc.



(19.11)

mp 102 °C

$$2C_5H_6 + NiCl_2{\bullet}6H_2O + 10KOH \xrightarrow[\text{in dimethoxyethane}]{\text{room temp, 30 min}} (C_5H_5)_2Ni + 2KCl + 8KOH{\bullet}H_2O \quad (19\text{-}12)$$

55 - 57 %
Cp_2Ni
mp 173 - 174 °C
sol. in most organic solvents

19.3.4 REACTIONS WITH UNSATURATED ORGANONICKEL Π-COMPLEXES

Biscyclooctadiene nickel π-complexes ($(COD)_2Ni$) shown in eq. (19.10) is an 18-electron compound, and thus it is stable and soluble in organic solvents such as benzene and tetrahydrofuran, and furthermore its reactivity is high. It is available as a starting material for synthesis of organonickel compounds as shown in Scheme 19.1 [20].

On the other hand, nickelocene (Cp_2Ni) shown in eq. (19.12) is a 20-electron compound, but it is so stable as $(COD)_2Ni$, and soluble in organic solvents. Then, the nickelocene is also available as a reagent for synthesis of organonickel compounds as shown in Scheme 19.2 [9,20].

Besides $(COD)_2Ni$ and Cp_2Ni as the unsaturated nickel π-complexes, allylnickel compounds are also available as a starting material for synthesis of organonickel compounds, since these compounds are relatively stable and have a high reactivity as shown in eqs. (19.8) and (19.13) [29].

$$NiBr_2 + 2CH_2{=}C(CH_3)CH_2MgCl \longrightarrow$$

$$\xrightarrow[-80^\circ C\ -\ \text{room temp}]{C_6H_5\text{-}Me\ +\ 2HSiCl_3} (\eta^6\text{-}C_6H_5\text{-}Me)Ni(SiCl_3)_2 + 2CH_2{=}CMe_2 \quad (19.13)$$

60 %, based on $NiBr_2$

19.3.5 OTHERS

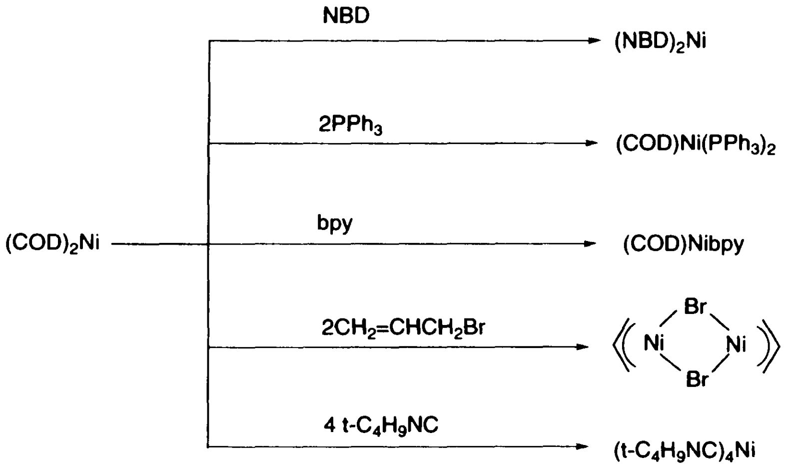
The other synthetic methods for organonickel compounds are reactions using organoalkali metal compounds such as Grignard reagents and organoaluminium compounds which are representative synthetic agents for the synthesis of typical organometallic compounds, as shown in eqs. (19.14)–(19.17) [20].

$$2MeLi + NiCl_2(PMe_3)_2 \xrightarrow{-70\ ^\circ C} Me_2Ni(PMe_3)_2 + 2LiCl \quad (19.14)$$

82 %

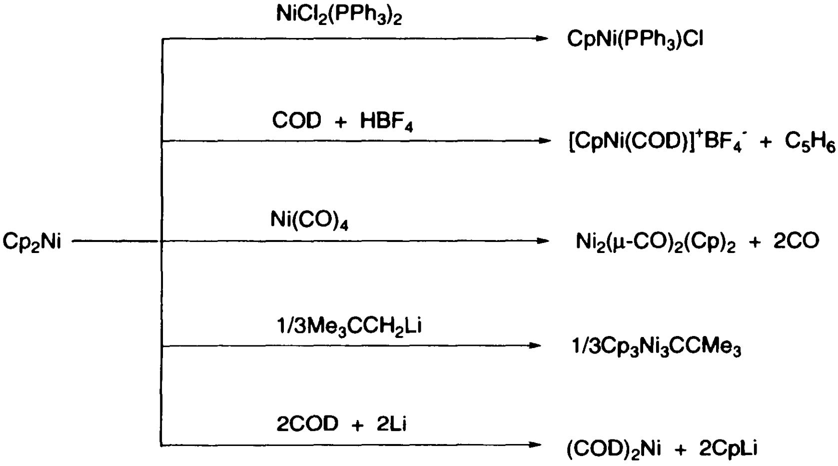
$$PhMgBr + NiBr_2(PEt_3)_2 \longrightarrow \text{trans-}PhNiBr(PEt_3)_2 \quad (19.15)$$

63 %



NBD = norbornadiene, bpy = bipyridyl

Scheme 19.1 [20]



Scheme 19.2 [9,20]

$$2HC{\equiv}CMgBr + NiBr_2(PBu_3)_2 \xrightarrow[\text{in THF}]{} \underset{50\ \%}{\text{trans-}(HC{\equiv}C)_2Ni(PBu_3)_2} \quad (19.16)$$

$$Et_2Al(OEt) + Ni(acac)_2 + 2,2'\text{-bipyridyl} \xrightarrow[\text{in ether}]{0\ ^\circ C\text{ - room temp, 8 hr}} \underset{55 - 65\ \%}{Et_2Ni(bpy)} \quad (19.17)$$

The vaporized nickel metal can react with aromatic compounds to afford η^6complexes. The reaction of toluene is shown in eq. (19.18) [20].

$$\mathrm{2Ni(g) + C_6H_5CH_3 + 2C_6F_5Br \longrightarrow (\eta^6\text{-}C_6H_5Me)Ni(C_6F_5)_2 + NiBr_2} \quad (19.18)$$

2.5 g
1g / hr

3 g, mp 137 - 140 °C

The nickel compounds of an acetylacetonate, isocyanate and phosphine react with gases such as nitrogen, oxygen and carbon dioxide to afford their complexes as shown in eqs. (19.19)–(19.21), respectively [20].

$$\mathrm{Ni(acac)_2 + N_2 + 4P(C_6H_{11})_3 \xrightarrow{AlMe_3} N_2Ni(P(C_6H_{11})_3)_4} \quad (19.19)$$

$$\mathrm{(t\text{-}BuNC)_4Ni + O_2 \longrightarrow (t\text{-}BuNC)_2Ni(O_2) + 2(t\text{-}BuNC)} \quad (19.20)$$

$$\mathrm{Ni(PEt_3)_3 + CO_2 \longrightarrow (CO_2)Ni(PEt_3)_2 + PEt_3} \quad (19.21)$$

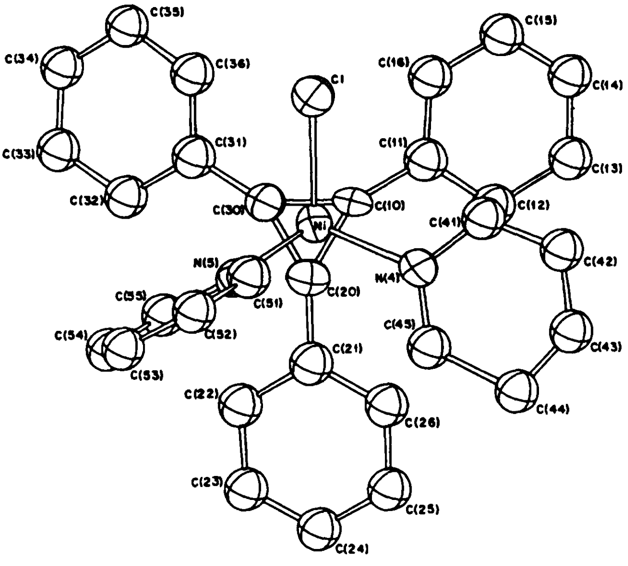
19.4 STRUCTURE OF ORGANONICKEL COMPOUNDS

As the outer shell electrons of nickel atom are $3d^84s^2$ as described above, it easily forms 18-electron compounds such as $Ni(CO)_4$ and $(COD)_2Ni$, in which the nickel atom is coordinated with four 2-electron donor groups. These compounds easily form tetrahedral structures of four coordination such as $(CO)_3Ni(P(t\text{-}Bu_3)_3$ and $(CO)_2Ni(PPh_3)_2$ [9]. $(\eta^3\text{-}Ph_3C_3)NiCl(py)_2$ shown in Figure 19.1 is also an 18-electron compound and forms a slightly distorted tetrahedral structure [30,31].

$(C_6F_5)NiBr(PPh_3)_2$ is a 16-electron compound, and since it is bonded with two bulky diphenylphosphines, these two groups are mutually located as *trans* and the nickel atom is in a slightly distorted square-planar coordination as shown in Figure 19.2 [32].

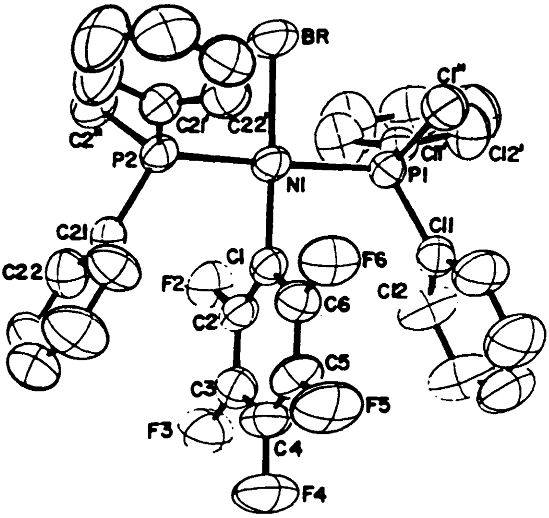
$(CO)NiI_2(PMe_3)_2$ shown in Figure 19.3 has a trigonal bipyramidal structure of five-coordination with the two axial positions occupied by trimethylphosphine groups [33,33a], and $\eta^2\text{-}(CH_2{=}CH_2)Ni(PPh_3)_2$ has a trigonal coordination if the ethylene group is regarded as a monodentate ligand [34–37].

Nickelocene (Cp_2Ni) is, as described above, a stable compound although it is a 20-electron compound. The solid form of this compound is not particularly air sensitive but in solution it must be handled in an inert atmosphere [9]. At room temperatures, crystalline nickelocene is isostructural with ferrocene and has a



distorted tetrahedron

Figure 19.1 Molecular structure of $(Ph_3C_3)NiCl(py)_2$ [30,31].



square-planar coordination

Figure 19.2 Molecular structure of trans-$(C_6F_5)NiBr(PPh_2Me)_2$ [32]

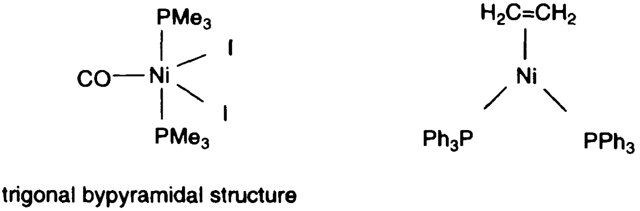


Figure 19.3 Structure of $(CO)NiI_2(PMe_3)_2$ and $(\eta^2\text{-}CH_2{=}CH_2)Ni(PPh_3)_2$ [33–34].

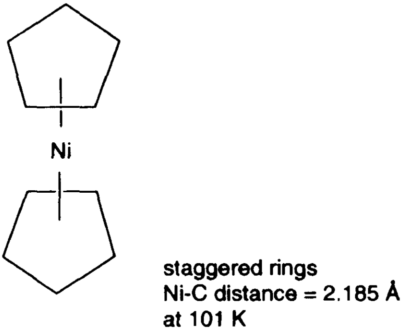


Figure 19.4 Structure of nickelocene (Cp_2Ni) [9]

staggered planar structure, and the nickelocene appears to have weaker metal–carbon bonds and a lower barrier to ring rotation than ferrocene [9,38].

Further, tripledecker compounds having cyclopentadienyl rings and tetradecker compounds of metallacarboranes having cobalt metals have also been reported [39–43].

$CpNi(\eta^3\text{-}C_3Ph_3)$ is an 18-electron compound having a cyclopropenyl and cyclopentadienyl ring. It also has a sandwich structure between the parallel cyclopentadienyl and triphenylcyclopropenyl rings, as shown in Figure 19.5 [44].

$(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_6)_2$ is an 18-electron compound in which the nickel atom is coordinated by a benzene ring as shown in Figure 19.6. A similar cobalt compound, $(\eta^6\text{-}C_6H_5CH_3)Co(C_6F_6)_2$, is a 17-electron compound and the benzene ring is in a planar structure, but the similar nickel compound has a boat structure as shown in Figure 19.6 [44a,44b].

The nitrogen atoms in $((C_6H_{11})_3P)_2Ni\text{-}N_2\text{-}Ni(P(C_6H_{11})_3)_2$ shown in eq. (19.22) have an end-on structure as shown in Figure 19.7. When there is nitrogen in the reaction system, an equilibrium state is reached as shown in eq. (19.23). However, by adding argon gas to the reaction system, $Ni(P(C_6H_{11})_3)_2$ is yielded with nitrogen dissociation [20,45,46].

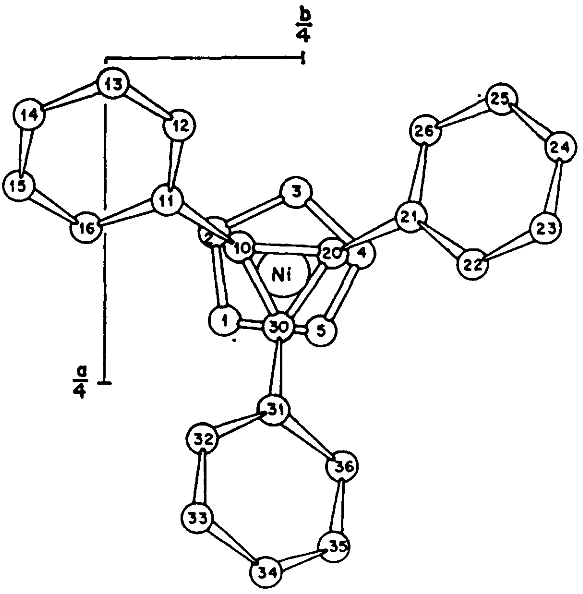


Figure 19.5 Molecular structure of (η^5-cyclopentadienyl-η^3-triphenylcyclopropenyl nickel ($CpNi(C_3Ph_3)$) [44].

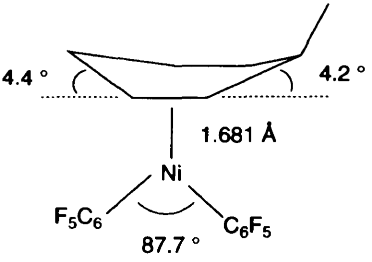


Figure 19.6 Molecular structure of (η^6-C_6H_5-CH_3)$Ni(C_6F_5)_2$ [44a].

$$(C_2H_4)Ni(P(C_6H_{11})_3)_2 \quad + \quad P(C_6H_{11})_3 \xrightarrow[-\,C_2H_4]{100\ ^\circ C} Ni(P(C_6H_{11})_3)_3$$

$$\xrightarrow{N_2,\ 25\ ^\circ C} ((C_6H_{11})_3P)_2Ni\text{ -}N_2\text{- }Ni(P(C_6H_{11})_3)_2 \qquad (19.22)$$

$$((C_6H_{11})_3P)_2Ni\text{ -}N_2\text{- }Ni(P(C_6H_{11})_3)_2 \rightleftharpoons N_2Ni(P(C_6H_{11})_3)_2 + Ni(P(C_6H_{11})_3)_2 \qquad (19.23)$$

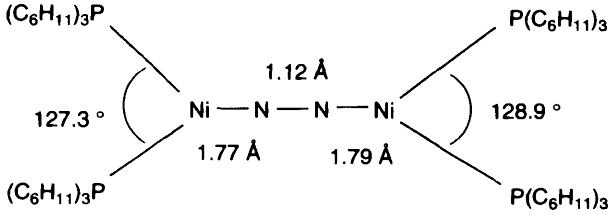
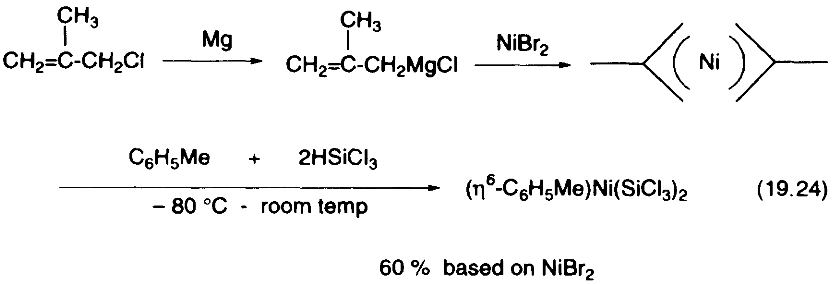


Figure 19.7 Molecular structure of $((C_6H_{11})_3P)_2\text{-}Ni_2\text{-}(P(C_6H_{11})_3)_2)$ [46].

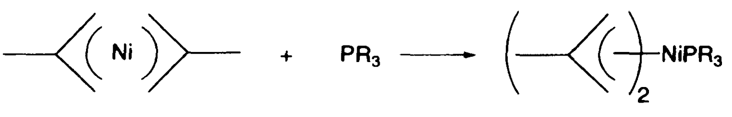
19.5 REACTIONS OF ORGANONICKEL COMPOUNDS

19.5.1 SUBSTITUTION REACTIONS

Nickel compounds readily react with carbon–carbon unsaturated compounds such as olefins, dienes, allyl and aromatic compounds and they are liable to afford stable π-complexes. These π-complexes have high reactivities. In particular, the π-complexes, which are not 18-electron complexes, are liable to afford 18-electron complexes by substitution reactions as shown in eqs. (19.24)–(19.29) [9,27,29,47–51].



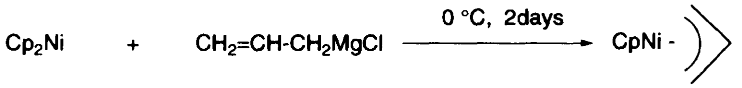
(19.24)



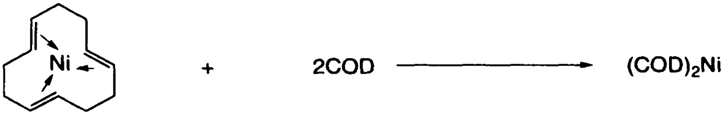
(19.25)

$PR_3 = PMe_3, PCy_3, PPh_3$

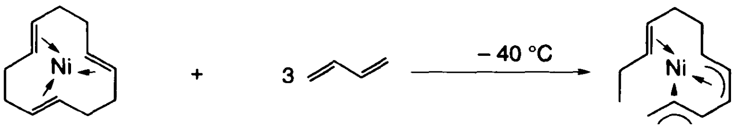
$$Cp_2Ni + NiBr_2 + AsPh_3 \xrightarrow[\text{in THF}]{50\,^\circ\text{C, 3hr}} CpNi(AsPh_3)Br \qquad (19.26)$$



(19.27)



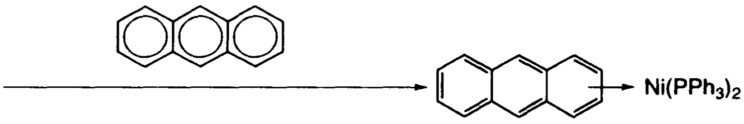
(19.28)



(19.29)

Recently, reactive alkylnickel compounds are synthesized by reactions of nickel phosphines with alkyllithium compounds, and they react with aromatic compounds without isolating them in the reaction system to afford the π-complexes as shown in eq. (19.30) [52].

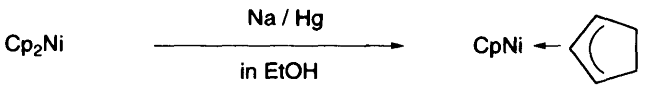
$$(Ph_3P)_2Ni \quad + \quad 2MeLi \longrightarrow (Ph_3P)_2NiMe_2$$



(19.30)

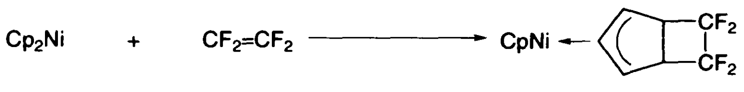
room temp 49.5 %
photochemicaly 74.5 %

Further, the formation reaction of 18-electron compounds proceeds by reduction or addition reactions as shown in eqs. (19.31) and (19.32) [53,54].



(19.31)

mp 43 °C

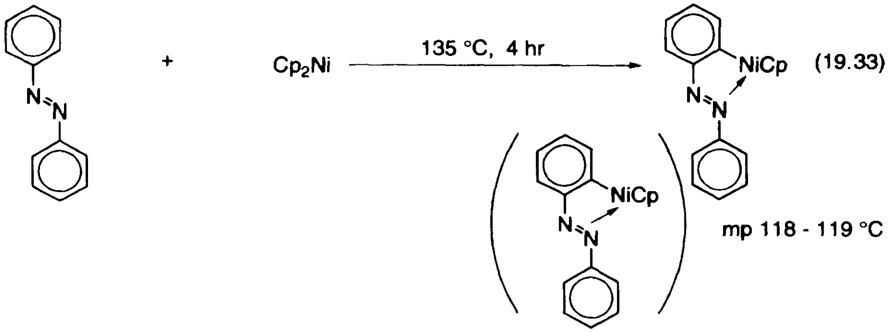


(19.32)

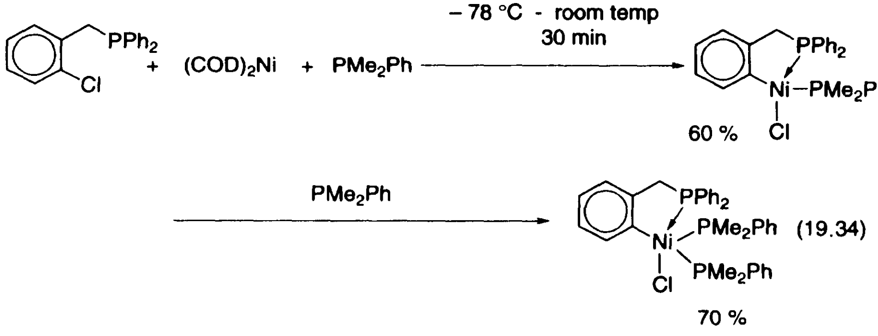
mp 93 - 94 °C

19.5.2 CYCLOMETALATIONS

Cyclometalations easily proceed to give many kinds of organometallic compounds, and these are liable to form mainly five-membered rings [55]. Orthometalation is one representative cyclometalation. The reaction shown in eq. (19.33) is the first reaction of orthometalation published 1963 [56]. It was considered in 1963 that the intramolecular coordination structure is formed since the nickel atom is coordinated by the π-electrons of the nitrogen–nitrogen double bond. But, afterwards, the ring structure was corrected to the structure where the nickel atom is coordinated by the lone pair electrons on the nitrogen atom, from many X-ray diffraction studies on other cyclometalated azobenzene complexes.



Organonickel compounds react with phosphines to form the five-membered ring compounds as shown in eq. (19.34). This compound has a distorted square-planar geometry, and is liable to react with another phosphine to form 18-electron compounds since it is a 16-electron compound [57].



Many other five-membered ring compounds have been synthesized as shown in Figure 19.8 [55,58–60].

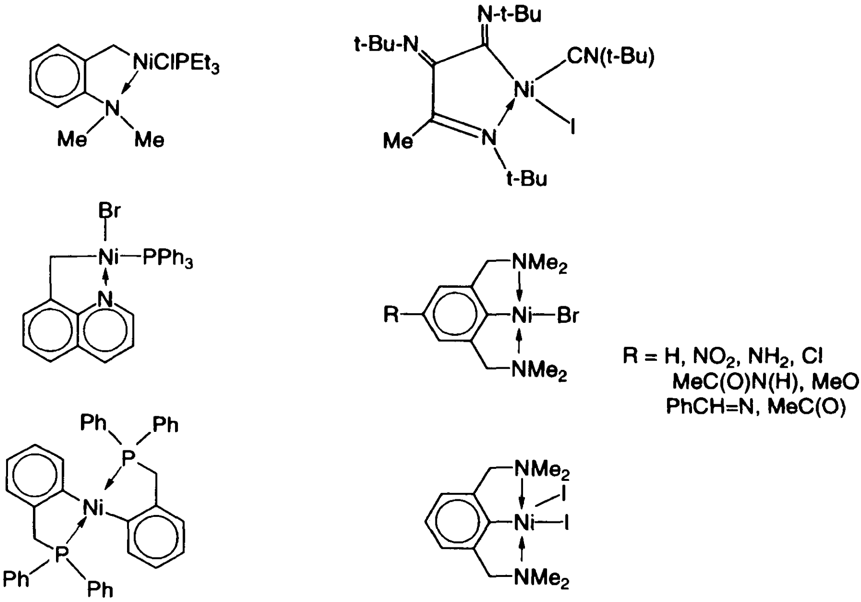


Figure 19.8 Organonickel intramolecular-coordination compounds containing five-membered ring structures [55,58–60].

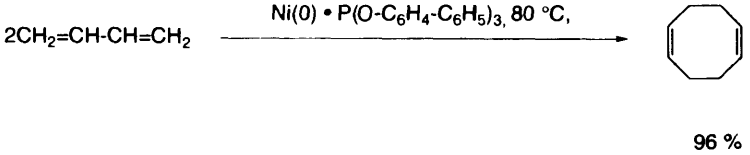
19.5.3 ORGANIC SYNTHESES WITH ORGANONICKEL COMPOUNDS

As described above, nickel compounds are liable to afford the π-complex with compounds having a carbon–carbon unsaturated bond such as olefins, acetylenes, allyl and aryl compounds, and further the nickel compounds are also liable to afford σ-complexes with alkyl or aryl compounds.

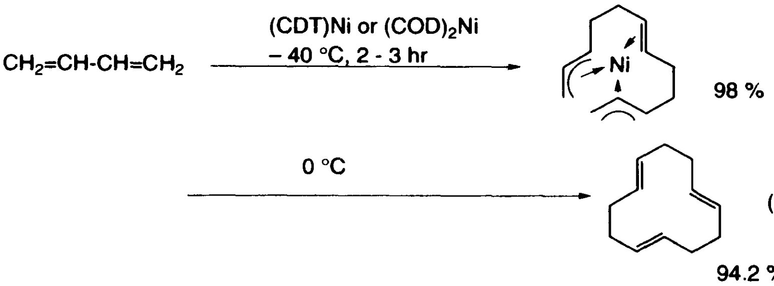
These nickel compounds have high reactivities and high selectivities to substrates and are easily handled in experimental operations. Then, these compounds are widely available as reagents and catalysts for organic syntheses [61–72]. In particular, the production of acrylic acid by Reppe reactions, the production of butene by the dimerization of ethylene, and the synthesis of 1,5-cyclooctadiene or 1,5,9-cyclododecatriene by the dimerization or trimerization of butadiene, are well known as reactions using nickel catalysts, shown in eqs. (19.35)–(19.38) [61,65,72–77].

$$HC{\equiv}CH + CO + MeOH \xrightarrow{Ni(CO)_4} CH_2{=}CHCOOMe \quad (19.35)$$

$$2CH_2{=}CH_2 \xrightarrow{Ni(acac)\text{ - }Et_3Al} CH_2{=}CH\text{-}CH_2CH_3 \quad (19.36)$$



(19.37)



(19.38)

19.5.3.1 Carbonylation

The carbonylations shown in eq. (19.35), are well known as one of the Reppe reactions, and the generalized reaction is shown in eq. (19.39). The carbonylations using the nickel catalysts are not only carried out with acetylenes but also with olefins or alcohols, and various kinds of compounds are produced by these reactions as shown in eqs. (19.39)–(19.41) [72].

$$\mathrm{HC{\equiv}CH + CO + HY \xrightarrow{[Ni]} CH_2{=}CHCOY} \quad (19.39)$$

$$\mathrm{RCH_2{=}CH_2 + CO + HY \xrightarrow{[Ni]} RCH_2CH_2COY} \quad (19.40)$$

$$\mathrm{RCH_2OH + CO \xrightarrow{[Ni]} RCH_2COOH} \quad (19.41)$$

$$\mathrm{Y = OH, OR, NR_2, RS, OOCR}$$

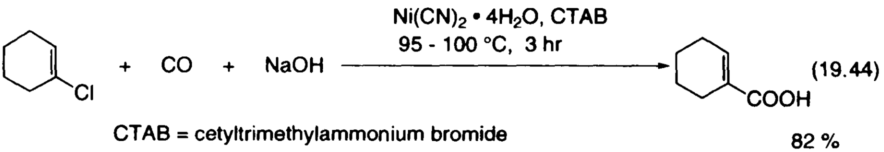
Acrylic acid and its esters formed by the reaction as shown in eq. (19.39) had been produced until the end of the 1960s. But now they are produced by the oxidation of propene. For the production of acetic acid by the carbonylation of methyl alcohol shown in eq. (19.41), nickel catalysts were at first used, but afterwards the rhodium catalysts as described previously in Chapter 18 have been used. However, even now nickel catalysts are used in the production of propionic acid by the carbonylation of ethylene shown in eq. (19.40) [72].

Carbonylations are liable to proceed with various kinds of halides as shown in eqs. (19.42)–(19.44). On the other hand, the carbonylation is able to proceed only with the excess of $Ni(CO)_4$ without using carbon monoxide as shown in eq. (19.45)

[78–81]. Double carbonylations and the other various kinds of carbonylations have been reported [65,82–85].

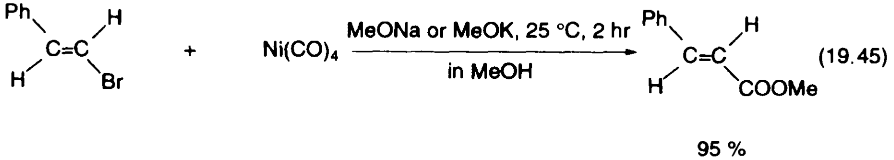
$$2PhCH_2Br \quad + \quad CO \xrightarrow[\text{in DMF}]{Ni(CO)_4,\ 50 - 60\ °C,\ 50\ hr} \underset{93\ \%}{PhCH_2COCH_2Ph} \qquad (19.42)$$

$$Ph\text{-}I \quad + \quad CO \quad + \quad NaOH \xrightarrow{Ni(CN)_2 \bullet 4H_2O,\ 90\ °C,\ 16.5\ hr} \underset{80\ \%}{PhCOOH} \qquad (19.43)$$



(19.44)

CTAB = cetyltrimethylammonium bromide



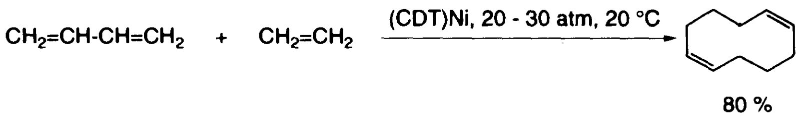
(19.45)

19.5.3.2 Oligomerization of Unsaturated Hydrocarbon

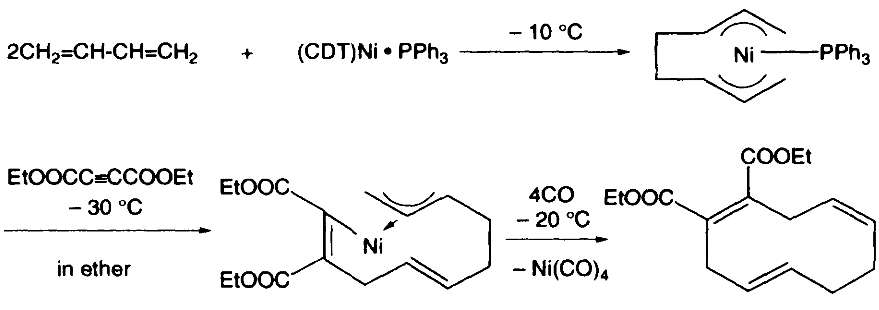
As described above, nickel is liable to form π-coordination with unsaturated hydrocarbons as shown in Figures 19.3–19.6. By taking advantage of the readiness of these π-coordination formation reactions, oligomerizations such as dimerization and trimerization, cyclizations, polymerizations and coupling reactions of nickel compounds with unsaturated compounds are liable to proceed as shown in eqs. (19.36)–(19.38). For example, the coupling reaction, coupling cyclization and intramolecular cyclization are shown in eqs. (19.46)–(19.49). These reactions are considered to proceed via π-coordination of unsaturated bonds such as double bonds, tripled bonds and allyl bonds [49,65, 86–91].

$$2HC{\equiv}CH \quad + \quad CH_2{=}CHCOOMe \xrightarrow[70\ °C,\ 50\ -\ 200\ psi,\ 6.5\ hr]{Ni(CO)_4,\ PPh_3,\ hydroquinone}$$

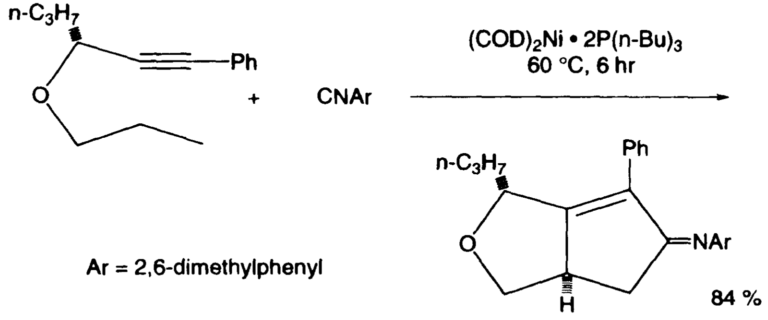
$$\underset{83\ \%}{CH_2{=}CH\text{-}CH{=}CH\text{-}CH{=}CHCOOMe} \qquad (19.46)$$



(19.47)



(19.48)

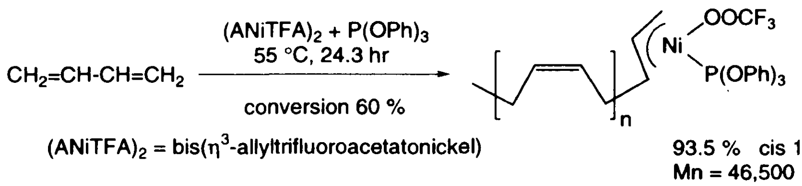


(19.49)

A bisallylnickel compound, which is a dimer of butadiene, is isolated by the reaction with nickel phosphine compounds as shown in eq. (19.48). It is also considered to be the intermediate of the compound shown in eq. (19.47). Further, it reacts with acetylene compounds at low temperatures, and subsequently reacts with carbon monoxide to give the ten-membered ring compound by elimination of nickel and simultaneous cyclization [91].

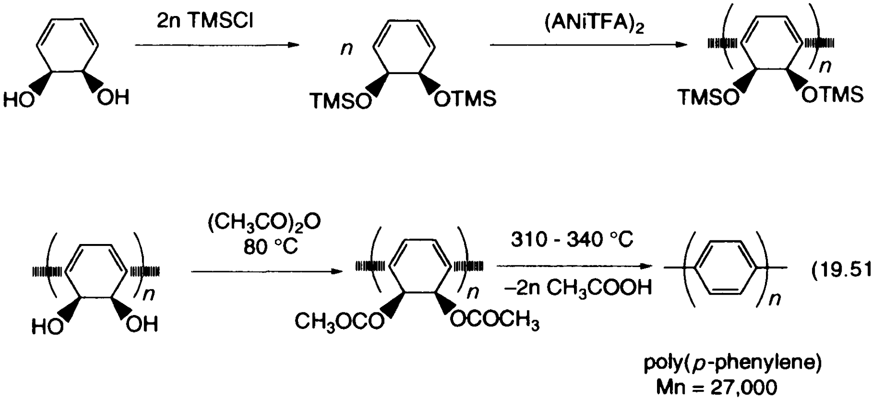
19.5.3.3 Polymerization

Dienes or olefins are polymerized in the presence of a π-allylnickel complex and a phosphate as catalysts to afford the polymers having a π-allyl group at the end position as shown in eq. (19.50). Then they are able to easily copolymerize with styrene or isocyanates [61,72,92–96]. Further, the polymerization of isocyanate and cyclohexadiene has been tried in the presence of nickel catalysts [94,95].



(19.50)

The siloxy compound of cyclohexadiene is able to polymerize as shown in eq. (19.51). However, it is difficult to dehydrogenate the siloxy polymers by heating, but their acetoxy compounds are able to be dehydrogenated at 310–340 °C to afford a high molecular weight poly-*p*-phenylene [95,95a].



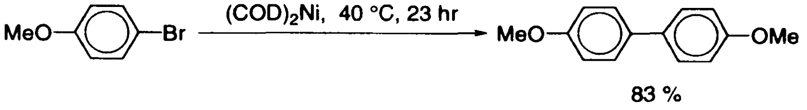
(19.51)

19.5.3.4 Coupling Reactions with Organic Halides

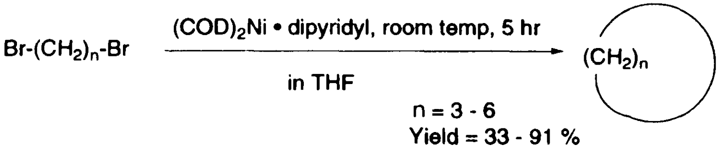
Nickel compounds such as $Ni(CO)_4$, $(COD)_2Ni$ and $Ni(PPh_3)_4$ are liable to react with unsaturated compounds such as monoolefins, dienes and acetylene and these are also liable to proceed via oxidative addition followed by the coupling reaction as shown in eq. (19.52).

$$\mathrm{RX} + \mathrm{Ni(0)} \longrightarrow \mathrm{R-Ni-X} \xrightarrow{\mathrm{R'X}} \mathrm{R-R'} + \mathrm{NiX_2} \quad (19.52)$$

For example, an ordinary coupling reaction of monohalide proceeds in the presence of a nickel-compound as shown in eq. (19.53) [96]. On the other hand, on a dihalide, the cyclization reaction proceeds as shown in eq. (19.54) [97].

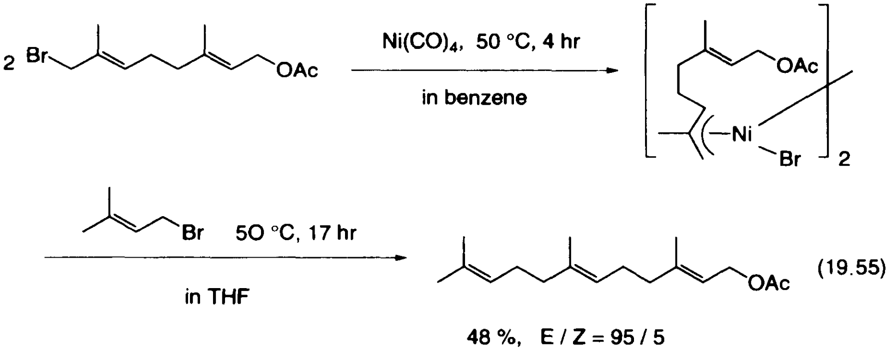


(19.53)



(19.54)

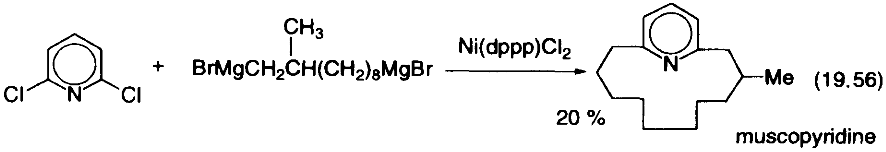
Further, (*E*,*E*) farnesyl acetate is selectively synthesized by the coupling reaction of halides as shown in eq. (19.55) [98,99].



19.5.3.5 Others

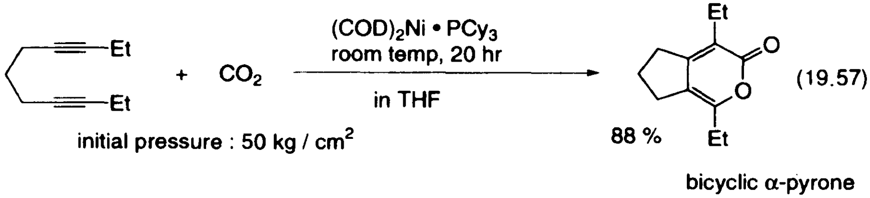
Coupling reactions with organic halides [62,71], cyclization addition of acetylenes with carbon dioxide, hydrogenations, reductions, oxidations, alkoxylations, aminations and insertions [100] have been reported as using nickel compounds.

The coupling reactions of Grignard reagents with organic halides were described in Chapter 4, and the production of muscopyridine, which is one of the odoriferous constituents of natural musk from the musk deer, by this coupling reaction is also shown in eq. (19.56) [101].



$Ni(dppp)Cl_2$ = dichloro(1,3-bis(diphenylphosphino)propanen)nickel(II)

The cyclization additions of acetylenes with carbon dioxide are the reactions to form the bicyclic compounds such as alkylene and heterocyclic ring (e.g., 2-pyrone ring) compounds, one of the reactions being shown in eq. (19.57) [68,102,103].



REFERENCES

[1] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.

[2] *Kagaku Binran Ooyohen*, Japan Chemical Society, Maruzen, Tokyo, p. 268, 1980.

[3] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., John Wiley, New York, vol.15, p. 787, 1980.

[4] *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, vol.A17, p. 157, 1990.

[5] *Kagaku Daijiten*, Tokyo Kagaku Doojin, Tokyo, p. 1677, 1989.

[6] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, 4th ed., p. 934, 1987.

[7] *Sekai Dai Hyakkajiten*, Heibonsha, Tokyo, vol.21, p. 349, 1988.

[8] *Sekai Kagaku Daijiten Technopia (Encyclopedia of Science and Technology)*, Kodansha, Tokyo, vol.13, p. 438, 1977.

[9] P.W. Jolly, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.6. p. 1, 1982.

[10] W.L. Gilliland and A.A. Blanchard, *Inorg. Synth.*, **2** (1946) 234.

[11] D.R. Fahey and J.E. Mahan, *J. Am. Chem. Soc.*, **99** (1977) 2501.

[12] H.-F. Klein and H.H. Karsch, *Chem. Ber.*, **109** (1976) 2524.

[13] G. Huttner, O. Orama and V. Bejenke, *Chem. Ber.*, **109** (1976) 2533.

[14] H.-F. Klein, *Angew. Chem.*, **85** (1973) 403.

[15] H.-F. Klein, *Angew. Chem. Int. Ed. Engl.*, **19** (1980) 362.

[16] T. Saruyama, T. Yamamoto and A. Yamamoto, *Bull. Chem. Soc. Japan*, **49** (1976) 546.

[17] T. Kohara, S. Komiya, T. Yamamoto and A. Yamamoto, *Chem. Lett.*, (1979)1513.

[18] L. Sacconi, P. Dapporto and P. Stoppioni, *J. Organomet. Chem.*, **116** (1976) C33.

[19] N.W. Barnett, *J. Organomet. Chem.*, **21** (1970) 477.

[20] *Jikken Kagaku Kouze 18, 4th ed., Yuki Kinzoku Sakutai*, Japan Chem. Soc. ed., Maruzen, Tokyo, p. 369, 1991.

[21] E.J. Corey and M.F. Semmelhack, *J. Am. Chem. Soc.*, **89** (1967) 2755.

[22] K. Sato, S. Inoue and K. Saito, *J. Chem. Soc. Perkin Trans. 1*, (1973)2289.

[23] W.C. Seidel and L.W. Gosser, *Inorganic Syntheses*, **15** (1974) 9.

[24] R.A. Schunn, *Inorganic Syntheses*, **15** (1974) 5.

[25] G. Wilke, *Angew. Chem.*, **72** (1960) 581.

[26] W.L. Jolley and D.J. Chazan, *Inorganic Syntheses*, **11** (1968) 123.

[27] Y. Kiso, K. Tamao and M. Kumada, *J. Organomet. Chem.*, **76** (1974) 105.

[28] A. Schott, H. Schott, G. Wilke, J. Brandt, H. Hoberg and E.G. Hoffmann, *Liebigs Ann. Chem.*, (1973)508.

[29] S.-B. Choe and K.J. Klabunde, *Organometallic Syntheses*, R.B. King and J.J Eisch ed., Elsevier, Amsterdam, vol.3, p. 153, 1986.

[30] D.L. Weaver and R.M. Tuggle, *J. Am. Chem. Soc.*, **91** (1969) 6506.

[31] R.M. Tuggle and D.L. Weaver, *Inorg. Chem.*, **10** (1971) 2599.

[32] M.R. Churchill, K.L. Kalra and M.V. Veidis, *Inorg. Chem.*, **12** (1973) 1656.

[33] M. Pankowski and M. Bigorgne, *J. Organomet. Chem.*, **35** (1972) 397.

[33a] C. Saint-Jolly, A. Mari, A. Gleizes, M. Dartiguenave, Y. Dartiguenave and J. Galy, *Inorg. Chem.*, **19** (1980) 2403.

[34] C.D. Cook, C.H. Koo, S.C. Nyburg and M.T. Shiomi, *J. Chem. Soc. Commun.*, (1967)426.

[35] C. Krüger and Y.-H. Tsay, *J. Organomet. Chem.*, **34** (1972) 387.

[36] R.S. Dickson and J.A. Ibers, *J. Organomet. Chem.*, **36** (1972) 191.

[37] K. Jonas, K.R. Pörschke, C. Krüger and Y.-H. Tsay, *Angew. Chem. Int. Ed. Engl.*, **15** (1976) 621.

[38] K.W. Barnett, *J. Organomet. Chem.*, **78** (1974) 139.

[39] E. Dubler, M. Textor, H.-R. Oswald and A. Salzer, *Angew. Chem.*, **86** (1974) 125.

[40] A. Salzer and H. Werner, *Angew. Chem.*, **84** (1972) 949.

[41] A. Salzer, T.L. Court and H. Werner, *J. Organomet. Chem.*, **54** (1973) 325.

[42] H. Werner, *Angew. Chem.*, **89** (1977) 1.

[43] J.R. Pipal and R.N. Grimes, *Organometallics*, **12** (1993) 4459.

[44] R.M. Tuggle and D.L. Weaver, *Inorg. Chem.*, **10** (1971) 1504.

[44a] L.J. Radonovich, K.J. Klabunde, C.B. Behrens, D.P. McCollor and B.B. Anderson, *Inorg. Chem.*, **19** (1980) 1221.

[44b] L.J. Radonovich, F.J. Koch and T.A. Albright, *Inorg. Chem.*, **19** (1980) 3373.

[45] P.W. Jolly and K. Jonas, *Inorganic Syntheses*, **15** (1974) 29.

[46] P.W. Jolly, K. Jonas, C. Krüger and Y.-H. Tsay, *J. Organomet. Chem.*, **33** (1971) 109.

[47] H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida and N. Hagihara, *J. Organomet. Chem.*, **6** (1966) 86.

[48] W.R. McClellan, H.H. Hoehn, H.N. Cripps, E.L. Muetterties and B.W. Howk, *J. Am. Chem. Soc.*, **83** (1961) 1601.

[49] G. Wilke, *Angew. Chem.*, **75** (1963) 10.

[50] G. Wilke, M. Krömer and B. Bogdanovic, *Angew. Chem.*, **73** (1961) 755.

[51] G.N. Schrauzer, *Adv. Organomet. Chem.*, **2** (1964) 1.

[52] A. Stanger and A. Shazar, *J. Organomet. Chem.*, **458** (1993) 233.

[53] M. Dubeck and A.H. Filbey, *J. Am. Chem. Soc.*, **83** (1961) 1257.

[54] D.W. McBride, R.L. Pruett, E. Pitcher and F.G. A. Stone, *J. Am. Chem. Soc.*, **84** (1962) 497.

[55] I. Omae, *Organometallic Intramolecular-coordinatin Compounds*, *J. Organometallic Chemistry Library 18*, Elsevier, Amsterdam, 1986.

[56] J.P. Kleiman and M. Dubeck, *J. Am .Chem. Soc.*, **85** (1963) 1544.

[57] G. Muller, D. Panyella, M. Rocamora, J. Sales, M. Font-Bardia and X. Solans, *J. Chem. Soc. Dalton Trans.*, (1993)2959.

[58] L.A. van de Kuil, H. Luitjes, D.M. Grove, J.W. Zwikker, J.G.M. van der Linden, A.M. Roelofsen, L.W. Jenneskens, W. Drenth and G. van Koten, *Organometallics*, **13** (1994) 468.

[59] G. van Koten, *Pure Appl. Chem.*, **61** (1989) 1681.

[60] D.M. Grove, G. van Koten and R. Zoet, *J. Am. Chem. Soc.*, **105** (1983) 1379.

[61] P.W. Jolly, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol.8, p. 613, 1982.

[62] I. Yamamoto ed., *Yuki Kinzoku Kagoubutsu, Goseiho oyobi Riyouhou*, Tokyo Kagaku Dojin, Tokyo, p. 218, 1991.

[63] *Jikken Kagaku Kouza 25, 4th ed., Yuki Gosei VII, Yuki Kizoku Shiyaku niyoru Gosei*, Chemical Society of Japan ed., Maruzen, p. 353, 1991.

[64] P. Heimbach, P.W. Jolly and G. Wilke, *Adv. Organomet. Chem.*, **8** (1970) 29.

[65] G.P. Chiusoli and G. Salemo, *Adv. Organomet. Chem.*, **17** (1979) 195.

[66] B. Bogdanovic, *Adv. Organomet. Chem.*, **17** (1979) 105.

[67] K. Tamao, K. Kobayashi and Y. Ito, *Yuki Goesi Kagaku Kyokaishi*, **48** (1990) 381.

[68] T. Tsuda, T. Kiyoi, N. Hasegawa and T. Saegusa, *Yuki Gosei Kagaku Kyokaishi*, **48** (1990) 362.

[69] M. Iyoda, *Yuki Gosei Kagaku Kyokaishi*, **48** (1990) 370.

[70] J. Tsuji, *Yuki Gosei okaeta Sen-i Kinzoku*, Kagaku Dojin, Kyoto, 1991.

[71] K. Tamao, *Kagaku Zokan*, **96** (1982) 65.

[72] W. Keim, *Angew. Chem. Int. Ed. Engl.*, **29** (1990) 235.

[73] W. Brenner, P. Heimbach, H. Hey, E.W. Müller and G. Wilke, *Liebigs Ann. Chem.*, **727** (1969) 161.

[74] B. Bogdanovic, P. Heimbach, M. Kröner, G. Wilke, E.G. Hoffmann and J. Brandt, *Liebigs Ann. Chem.*, **727** (1969) 143.

[75] P. Heimbach, J. Kluth, H. Schenkluhn and B. Weimann, *Angew. Chem. Int. Ed. Engl.*, **19** (1980) 570.

[76] P. Heimbach, J. Kluth, H. Schenkluhn and B. Weimann, *Angew. Chem. Int. Ed. Engl.*, **19** (1980) 569.

[77] H.W.B. Reed, *J. Chem. Soc.*, (1954)1931.

[78] E. Yoshisato and S. Tsutsumi, *J. Org. Chem.*, **33** (1968) 869.

[79] I. Amer and H. Alper, *J. Org. Chem.*, **53** (1988) 5147.

[80] H. Alper, I. Amer and G. Vasapollo, *Tetrahedron Lett.*, (1989)2615.

[81] E.J. Corey and L.S. Hegedus, *J. Am. Chem. Soc.*, **91** (1969) 1233.

[82] G.P. Chiusoli, S. Merzoni and G. Mondelli, *Tetrahedron Lett.*, (1964)2777.

[83] P. Koch and E. Perrotti, *J. Organomet. Chem.*, **81** (1974) 111.

[84] N.L. Bauld, *Tetrahedron Lett.*, (1963)1841.

[85] K. Younis and I. Amer, *Organometallics*, **13** (1944) 3120.

[86] T.L. Cairns, V.A. Englehardt, H.L. Hackson, G.H. Kalb and J.C. Sauer, *J. Am. Chem. Soc.*, **74** (1952) 5636.

[87] P. Heimbach and G. Wilke, *Liebigs Ann. Chem.* **727** (1969) 183.

[88] W. Brenner, P. Heimbach and G. Wilke, *Liebigs Ann. Chem.*, **727** (1969) 194.

[89] K. Tamao, K. Kobayashi and Y. Ito, *J. Am. Chem. Soc.*, **110** (1988) 1286.

[90] K. Tamao, K. Kobayashi and Y. Ito, *J. Org. Chem.*, **54** (1989) 3517.

[91] B. Büssemeier, P.W. Jolly and G. Wilke, *J. Am. Chem. Soc.*, **96** (1974) 4726.

[92] P. Hadjiandreou, M. Julémont and P. Teyssié, *Macromolecules*, **17** (1984) 2455.

[93] T.J. Deming, B.M. Novak and J.W. Ziller, *J. Am. Chem. Soc.*, **116** (1994) 2366.

[94] T.J. Deming and B.M. Novak, *J. Am. Chem. Soc.*, **115** (1993) 9101.

[95] D.L. Gin, V.P. Conticello and R.H. Grubbs, *J. Am .Chem. Soc.*, **114** (1992) 3167.

[95a] D.L. Gin , V.P. Conticello and R.H. Grubbs, *J. Am. Chem. Soc.*, **116** (1994) 10934.

[96] M.F. Semmelhack, P. Helquist, L.D. Jones, L. Keller, L. Mendelson, L.S. Ryono, J.G. Smith and R.D. Stauffer, *J. Am. Chem. Soc.*, **103** (1981) 6460.

[97] S. Takahashi, Y. Suzuki and N. Hagihara, *Chem. Lett.*, (1974)1363.

[98] K. Sato, S. Inoue and S. Morii, *Chem. Lett.*, (1975)747.

[99] K. Sato and S. Inoue, *Yuki Gosei Kagaku Kyokaishi*, **46** (1988) 318.

[100] M.A. Bennet and E. Wenger, *Organometallics*, **14** (1995) 1267.

[101] K. Tamao, S. Kodama, T. Nakatsuka, Y. Kiso and M. Kumada, *J .Am .Chem. Soc.*, **97** (1975) 4405.

[102] T. Tsuda, S. Morikawa, R. Sumiya and T. Saegusa, *J. Org. Chem.*, **53** (1988) 3140.

[103] Y. Inoue, T. Itoh, H. Kazama and H. Hashimoto, *Bull. Chem. Soc. Japan*, **53** (1980) 3329.

20 Organopalladium Compounds

20.1 INTRODUCTION

Recently, the largest number of articles on organometallic compounds have been published on organopalladium compounds, together with organosilicon compounds. In the studies or organopalladium compounds compared with other organometallic compounds, the number of studies on their synthesis or reactions are relatively few while the number of studies on organosynthetic reactions with inorganic palladium compounds are numerous. As these inorganic palladium compounds form organopalladium compounds as intermediates of the reaction system, their reactions are dealt with as reactions of organometallic compounds. Palladium compounds are used for their wide range of reactions since they have high selectivity. Tsuji [1–4] has published reports recently that the palladium compounds have been industrially used for the production of many chemicals, pharmaceuticals, perfumes, etc.

20.2 PALLADIUM

Palladium belongs to group 10 of the periodic table, the same as nickel, and its outer electronic configuration is $4d^{10}5s^0$. It exists as 0.0006 ppm in the Earth's crust and this is similar to gold (0.0011 ppm) and silver (0.07 ppm) [5,6].

Palladium is produced from an anode slime in the electrolytic refining of crude copper or nickel as described in Chapters 16 and 18, or from platinum ores. The raw materials are treated with aqua regia, with platinum, palladium and gold dissolved as chlorine complexes, and then ammonium chloride is added to the solution to precipitate as $(NH_4)_2PtCl_6$. Ammonium chloride and nitric acid are added to the mother liquor and heated to yield the crystal $(NH_4)_2PdCl_6$. The excess aqueous ammonia is added to the $(NH_4)_2PdCl_6$ crystal and is heated to reduce it and to dissolve it as $[Pd(NH_3)_4]^{2+}$. Hydrochloric acid is added to precipitate Pd as $[Pd(NH_3)_4]Cl_2$, and, 99.99% purity of palladium is obtained by heating $[Pd(NH_3)_4]Cl_2$ [7–10]. Properties of palladium are shown in Table 20.1.

Palladium is a silver white, ductile and malleable metal. Palladium readily takes up hydrogen as Pd_2H and the volume of hydrogen is 800 times or more of that of the metal. The hydrogen absorbed by palladium is activated. Therefore, palladium is excellent as a reductive catalyst. Oxygen reacts superficially at around 350°C to form an oxide coating (PdO) but this decomposes again at 790°C or higher temperatures. Fluorine, chlorine, sulfur, selenium, phosphorus, arsenic and silicon react

Table 20.1 Properties of palladium [5,7,8]

Property	Value
melting point, °C	1552
boiling point, °C	2940
crystal structure	face-centered cubic
density, 20°C, g/cm^3	12.02
specific heat at 0°C, J g^{-1}	0.244
linear coefficient of thermal expansion at 20°C, K^{-1}	11.1×10^{-6}
electrical resistivity at 20°C, μΩ·cm	9.9
hardness	
Mohs scale	4.8
Vickers hardness, annealed	37– 39
thermal conductivity, Wm^{-1} K^{-1}	75.3
mass susceptibility, cm^3 g^{-1}	5.23×10^{-6}

with Pd on heating. Palladium has the weakest resistance to acid of the platinum metals, easily dissolved in aqua regia, gradually dissolves in dilute nitric acid, dissolves in hydrochloric acid in the presence of air, and dissolves in boiling concentrated sulfuric acid [5,7–10]. As palladium is a lower price than platinum, it is used in alloy metals such as electrical contact points, bearing metals, dental and surgery materials, ornament precious metals, etc. Palladium is used for organosynthetic catalysts assuming the form of palladium black, palladium sponge and palladium colloid [5,7–10].

20.3 PREPARATION OF ORGANOPALLADIUM COMPOUNDS

There have been many studies on palladium compounds forming organopalladium compounds as intermediates by using $PdCl_2$, $Pd(acac)_2$ and $Pd(PPh_3)_4$, etc. as organosynthetic catalysts. But, this section shows the synthetic methods of stable organopalladium compounds, not liable intermediates. Basic reaction methods using the preparation of organopalladium compounds are the following nine reactions [11–13]

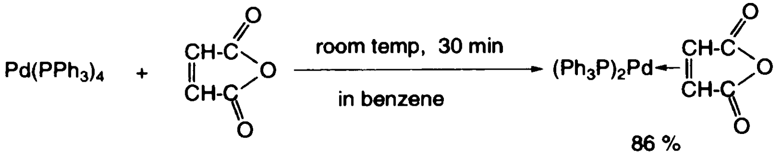
(1) Reactions with unsaturated hydrocarbons
(2) Reactions with unsaturated hydrocarbon palladium complexes
(3) Reactions with various kinds of organometallic compounds
(4) Carbonylations
(5) Oxidative additions with organic halides
(6) Direct reactions

(7) Reactions with nitrile palladium compounds or with isonitrile palladium compounds
(8) Cyclometalations
(9) Others

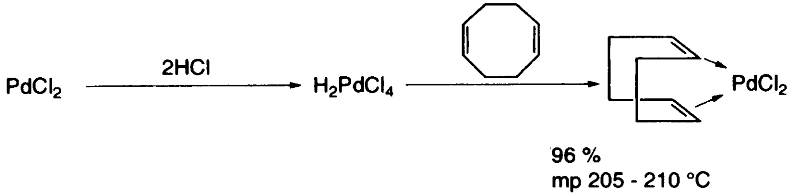
20.3.1 REACTIONS WITH UNSATURATED HYDROCARBONS

Palladium compounds are liable to react with unsaturated hydrocarbons such as monoolefins, diolefins, acetylenes and allyl compounds to afford their π-complexes. For example, reactions with monoolefins and diolefins are shown in eqs. (20.1)–(20.3) [14–17].

$$\mathrm{Pd(acac) + 2PPh_3 + CH_2{=}CH_2 \xrightarrow[\text{in mixture of toluene and ether}]{\mathrm{Et_2AlOEt},\ \text{room temp, 24 h}} \underset{75\ \%}{(CH_2{=}CH_2)Pd(PPh_3)_2}} \quad (20.1)$$

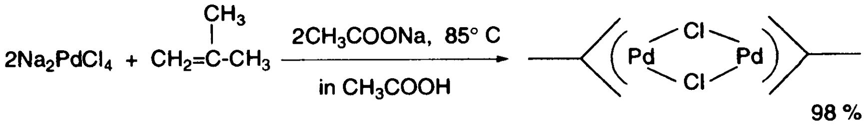


(20.2)

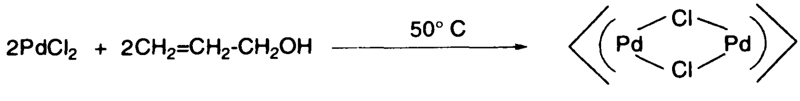


(20.3)

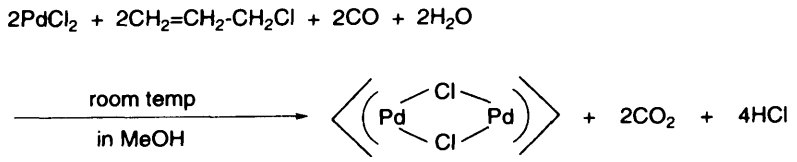
Allylpalladium compounds are prepared by reactions with 2-methylpropylene, allyalcohol or allylchloride as shown in eqs. (20.4)–(20.6) [18–21]. Examples of the π-complexes with cyclopentadiene and acetylene are shown in eqs. (20.7) and (20.8), respectively [22–24].



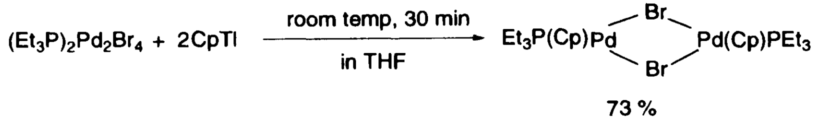
$+\ 2CH_3COOH\ +\ 6NaCl$ (20.4)



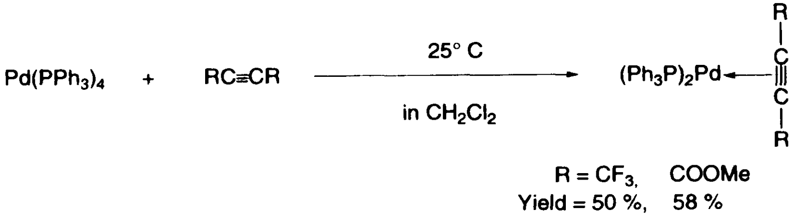
(20.5)



(20.6)



(20.7)

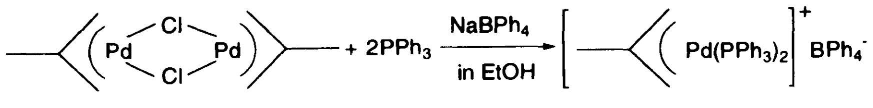


(20.8)

Recently, fullerene reacts with $Pd(PPh_3)_4$ to afford $C_{60}Pd(PPh_3)_2$ by the ligand exchange reaction of carbon–carbon unsaturated bond of fullerene with two phosphine groups. The coordination structure was determined by X-ray diffraction studies [25].

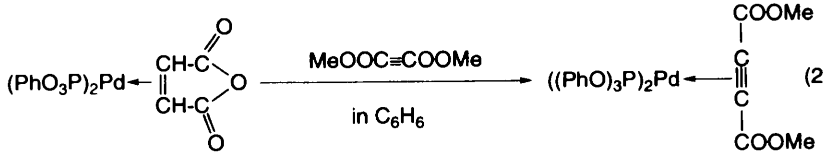
20.3.2 REACTIONS WITH UNSATURATED HYDROCARBON PALLADIUM COMPOUNDS

Unsaturated hydrocarbons such as alkenes, 1,5-cyclooctadiene, allyl compounds and cyclopentadienyl compounds easily react with palladium compounds to afford their π-complexes. These π-complexes are used as the raw materials for the syntheses of organopalladium compounds. For example, reactions are shown in eqs. (20.9)–(20.12) [26–31].

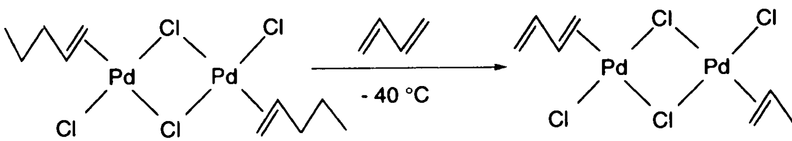


(20.9)

$$(COD)_2Pd + 3CH_2{=}CH_2 \longrightarrow (CH_2{=}CH_2)_3Pd \quad (20.10)$$

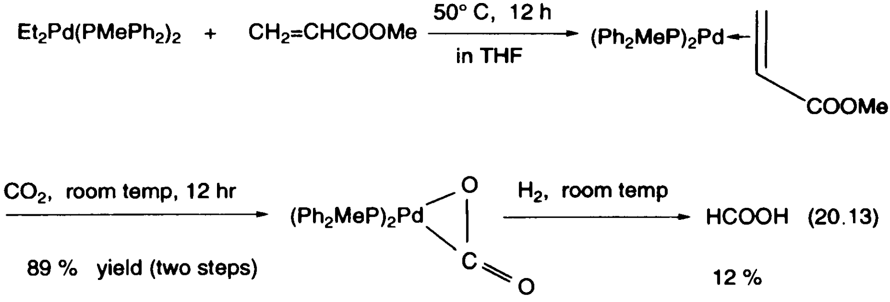


(20.11)



(20.12)

Recently, acrylic acid methylester palladium complexes are able to react with carbon dioxide. The substituted compound with carbon dioxide affords formic acid by reaction with hydrogen at room temperatures. Therefore, the reaction is the fixation of carbon dioxide by palladium compounds.

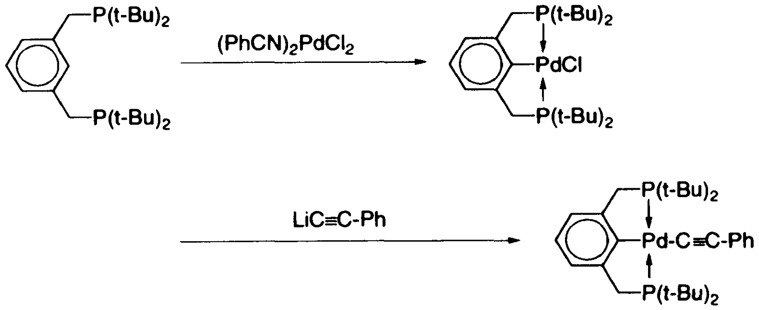


(20.13)

20.3.3 REACTIONS WITH VARIOUS KINDS OF ORGANOMETALLIC COMPOUNDS

Organopalladium compounds are prepared with organometallic compounds such as organoalkali metal compounds, Grignard reagents and organoaluminium compounds. For example, reactions are shown in eqs. (20.14)–(20.17) [32–35].

$$(Et_3P)_2PdCl_2 + 2PhLi \xrightarrow[\text{in ether}]{-75^\circ\text{ C - room temp}} Ph_2Pd(PEt_3)_2 \qquad (20.14)$$



(20.15)

$$MeMgBr + (Et_3P)_2PdBr_2 \xrightarrow[\text{in ether}]{-65^\circ\text{ C - room temp}} \underset{78\ \%}{MePdBr(PEt_3)_2} \qquad (20.16)$$

$$Pd(acac)_2 + 2PEt_3 + Me_2Al(OEt) \xrightarrow{0^\circ\text{ C, several h}} \underset{40\ \%}{Me_2Pd(PEt_3)_2} \qquad (20.17)$$

20.3.4 CARBONYLATIONS

Transition metals such as Mn, Fe, Ru, Co, Rh, Ni and their metal compounds easily react with carbon monoxide to afford their metal carbonyl compounds ($M_m(CO)_n$). But no correspond palladium compound ($Pd_m(CO)_n$) is isolated. However, if the palladium is coordinated by an electron-donating compound such as phosphine and SO_3F, the palladium atom is able to form stable compounds with carbon monoxide [36–49]. For example, palladium carbonyl compounds are prepared by the reaction of palladium phosphine with carbon monoxide or by the reaction of palladium compounds with phosphine in the presence of carbon monoxide as shown in eqs. (20.18) and (20.19) [39].

$$Pd(PPh_3)_4 + CO \xrightarrow[\text{in } C_6H_6]{\text{room temp, 3 min}} \underset{90\ \%}{Pd(CO)(PPh_3)_3} \qquad (20.18)$$

$$Pd(acac)_2 + 3PPh_3 + CO \xrightarrow{Et_3Al,\ -50^\circ - 10^\circ\text{ C}} \underset{70-80\ \%}{Pd(CO)(PPh_3)_3} \qquad (20.19)$$

On the other hand, with fluorosulfate compound, the carbonylation is shown in eq. (20.20) [42].

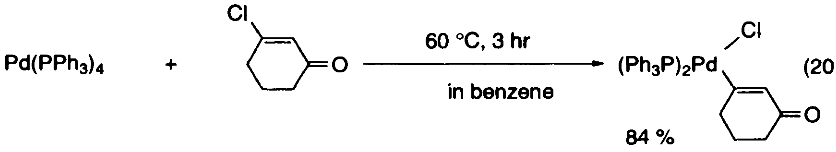
$$Pd_2(SO_3F)_6 \quad + \quad 5CO \xrightarrow{25\ ^\circ C,\ \sim 550\ Torr,\ 1\ h} 2Pd(CO)_2(SO_3F)_2 + CO_2 + S_2O_5F_2 \qquad (20.20)$$

20.3.5 OXIDATIVE ADDITION WITH ORGANIC HALIDES

Organopalladium compounds are prepared by the oxidative addition of organic halides to palladiumphosphine compounds as shown in eqs. (20.21)–(20.23) [13,40–43].

$$Pd(PPh_3)_4 \quad + \quad RX \longrightarrow Ph_3P\text{-}\overset{\displaystyle R}{\underset{\displaystyle X}{Pd}}\text{-}PPh_3 \qquad (20.21)$$

$$RX = MeI\ ,\ CH_2{=}CMeCH_2Cl,\ CH_3COCl,\ EtOCOCl,\ PhI$$



(20.22)

84 %

$$Pd(PPh_3)_4 \quad + \quad ClCH_2COPh \longrightarrow (Ph_3P)_2\overset{\displaystyle Cl}{Pd}CH_2COPh \qquad (20.23)$$

85 %

20.3.6 DIRECT REACTIONS

Palladium metal reacts with organic halides directly and organopalladium compounds are isolated by reaction with phosphine [44–48]. For example, organopalladium compounds are prepared by the reaction of organic halides with vaporized palladium or with metal slurry obtained by the reduction of palladium halide with an alkali metal as shown in eqs. (20.24)–(20.26). The last reaction shows higher yield.

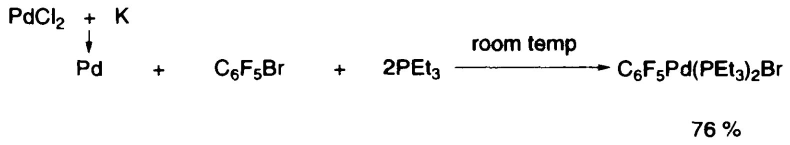
$$Pd \; + \; CF_3Br \xrightarrow{-196\ ^\circ C \quad -78\ ^\circ C,\ pump\text{-}off} (CF_3PdBr)_n \xrightarrow[in\ CH_2Cl_2]{PEt_3} trans\text{-}CF_3Pd(PEt_3)_2Br \qquad (20.24)$$

7 %, mp 96 - 97 °C

$$\mathrm{Pd} + \mathrm{C_6F_5Br} \xrightarrow{-196\ ^\circ\mathrm{C}\ -\ \text{room temp, pump-off}} (\mathrm{C_6F_5PdBr})_n$$

$$\xrightarrow{\mathrm{PPhMe_2}} \textit{trans-}\mathrm{C_6F_5Pd(PPhMe_2)_2Br} \qquad (20.25)$$

33 % (based on metal)



$$\mathrm{PdCl_2 + K \rightarrow Pd} + \mathrm{C_6F_5Br} + 2\mathrm{PEt_3} \xrightarrow{\text{room temp}} \mathrm{C_6F_5Pd(PEt_3)_2Br} \qquad (20.26)$$

76 %

20.3.7 REACTIONS WITH NITRILEPALLADIUMS OR WITH ISONITRILEPALLADIUMS

Nitrilepalladium or isonitrilepalladium is easily prepared in high yield by reaction with palladium halides or unsaturated palladium compounds as shown in eqs. (20.27)–(20.30) and these palladium compounds are used as the raw material for synthesis of other organopalladium compounds as shown in eqs. (20.31)–(20.34) [11,12,49–57].

$$\mathrm{PdCl_2} + 2\mathrm{PhCN} \xrightarrow{160\ ^\circ\mathrm{C},\ 20\ \mathrm{min}} \mathrm{(PhCN)_2PdCl_2} \qquad (20.27)$$

93 %

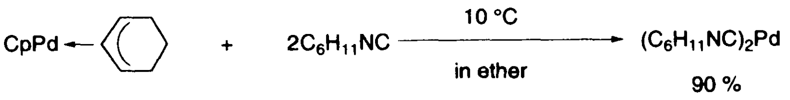
$$\mathrm{PdCl_2} + 2\text{t-BuNC} \xrightarrow[\text{in } \mathrm{C_6H_6}]{} (\text{t-BuNC})_2\mathrm{PdCl_2} \qquad (20.28)$$

quantitative yield

$$\mathrm{(CH_3CN)_2PdCl_2} + 2\mathrm{RCN} \xrightarrow{160\ ^\circ\mathrm{C},\ 20\ \mathrm{min}} \mathrm{(RCN)_2PdCl_2} \qquad (20.29)$$

$\mathrm{R = Ph,\ C_6H_{11}}$

quantitative yield



(20.30)

90 %

$$(\mathrm{PhCN})_2\mathrm{PdCl}_2 + \mathrm{C_4H_6} \xrightarrow[\text{in benzene}]{} (\mathrm{C_4H_6})\mathrm{PdCl}_2 + 2\mathrm{PhCN} \qquad (20.31)$$

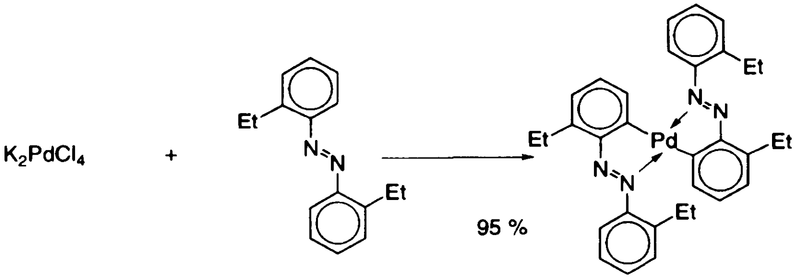
$$(t\text{-}\mathrm{BuNC})_2\mathrm{Pd} + \mathrm{MeI} \xrightarrow[\text{in hexane}]{0\ ^\circ\mathrm{C}} \underset{42\ \%}{\textit{trans}\text{-}\mathrm{Me(t\text{-}BuNC)_2PdI}} \qquad (20.32)$$

$$(t\text{-}\mathrm{BuNC})_2\mathrm{Pd} + \mathrm{CH_3COCl} \xrightarrow[\text{in toluene}]{0\ ^\circ\mathrm{C},\ 30\ \mathrm{min}} \underset{92\ \%}{(\mathrm{CH_3CO})(t\text{-}\mathrm{BuNC})_2\mathrm{PdCl}} \qquad (20.33)$$

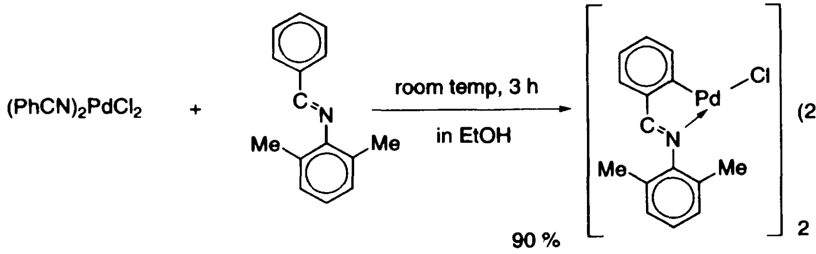
$$(t\text{-}\mathrm{BuNC})_2\mathrm{Pd} + \mathrm{O_2} \xrightarrow[\text{in ether}]{-30\ ^\circ\mathrm{C}} \underset{60\ \%}{(t\text{-}\mathrm{BuNC})_2\mathrm{PdO_2}} \qquad (20.34)$$

20.3.8 CYCLOMETALATIONS

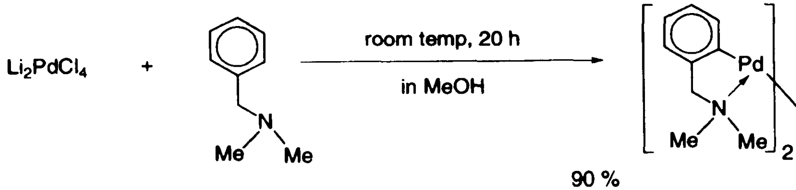
The cyclometalations of palladium compounds proceed with benzylidenanilines [58–85], azobenzenes [58,86–96], N,N-dimethylaminomethylbenzenes [61,93,94, 96–115], N,N-dimethylaminomethylnaphthalenes [61,116–112c], 8-methylquinolines [61,94,123–127b], N,N-dimethylmethylferrocenes [128,129], etc. [130–142e] to afford mainly five-membered ring compounds [143–145]. For example, cyclometalations are shown in eqs. (20.35)–(20.39) and the many structures of these products have been determined by X-ray diffraction studies.



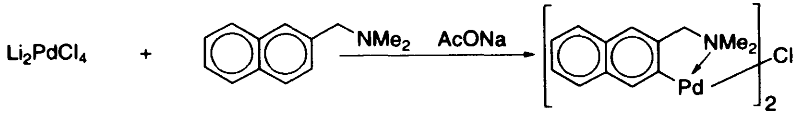
(20.35)



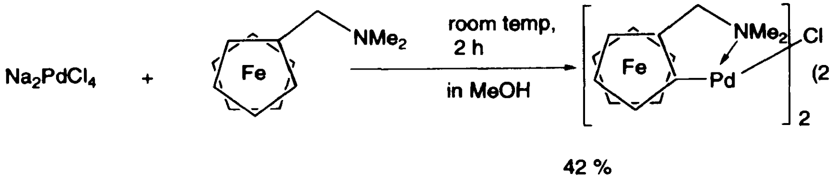
(20.36)



(20.37)



(20.38)



(20.39)

20.3.9 OTHERS

Acetylene compounds having a reactive hydrogen react with palladium compounds to afford the σ-compounds by substitution reaction as shown in eq. (20.40). But acetylene compounds not having a reactive hydrogen form π-complexes as shown in eq. (20.8) [146]. On the other hand, as described below, under some reaction coonditions, their dimeric cyclizations also proceed as shown in eq. (20.52) [147–154].

$$trans\text{-}(Et_3P)_2PdCl_2 \quad + \quad HC{\equiv}CR \longrightarrow trans\text{-}(Et_3P)_2Pd(C{\equiv}CR) \qquad (20.40)$$

$$\begin{array}{ll} R & = H, \quad Me, \quad CH_2OH \\ \text{Yield} & = 87\ \%, \ 70\ \%, \ 75\ \% \end{array}$$

20.4 STRUCTURES OF ORGANOPALLADIUM COMPOUNDS

There have been many reports on X-ray diffraction studies of organopalladium compounds. However, most of the structures are square-planar structure with four-coordination as shown in Figure 20.1 [155].

The structures of acetylene π-complexes (eq. (20.8)) are shown in Figure 20.2 [150]. Two carbons of the acetylene, two phosphorus atoms, and one palladium are approximately planar. It looks like three coordination structure. Each substituent upon acetylene is bent away from the methyl by about 35° from the C≡C bond axis by the effect of bulk triphenylphosphine group.

Me_3PdI·bpy obtained by the odixative addition of MeI to Me_2Pd·bpy forms the octahedral structure of six-coordination as shown in Figure 20.3 [157,158].

20.5 REACTIONS OF ORGANOPALLADIUM COMPOUNDS

Organopalladium compounds such as π-allypalladium compounds and 1,5-COD palladium compounds react with many compounds to afford various kinds of organopalladium compounds. The interesting reactions of organopalladium compounds are insertions and cyclic dimerizations.

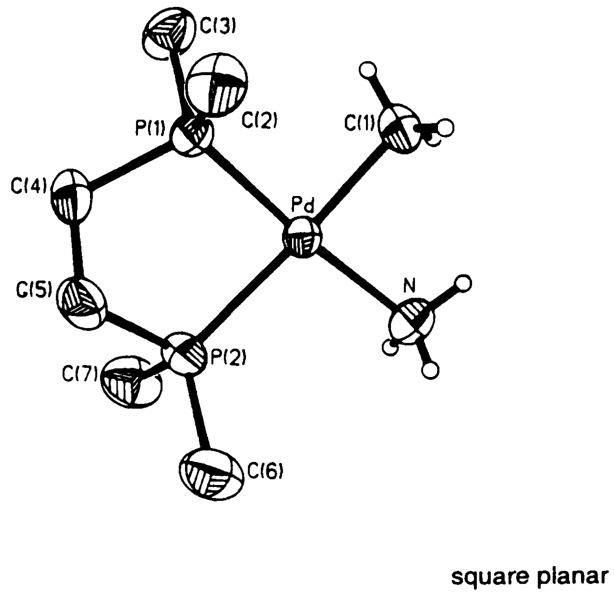
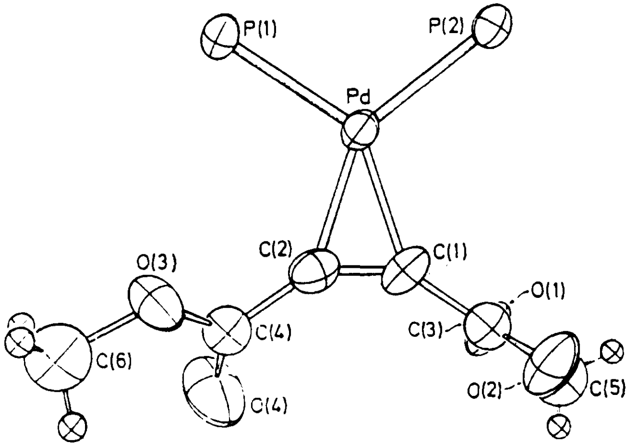
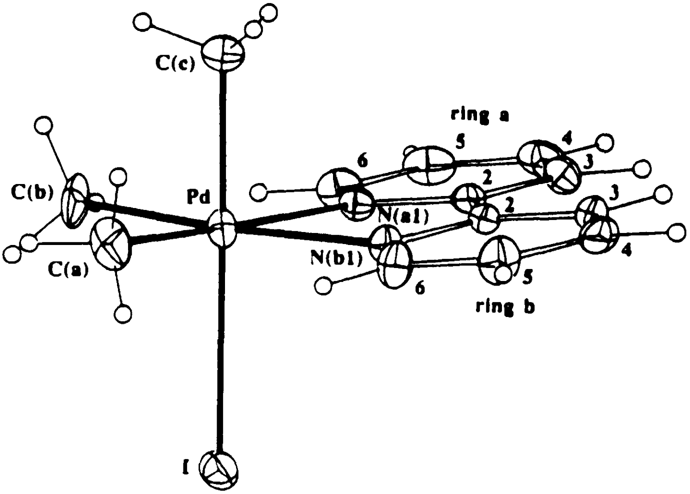


Figure 20.1 Structure of aminebis(dimethylphosphine)ethanemethylpalladium(II) cation [155].



P-Pd-P = 107.43 °
C(2)-C(1)-C(3) = 146.4 °
C(1)-C(2)-C(4) = 144.9 °

Figure 20.2 Structure of (dimethyl acetylenedicaboxylate)bis(trimethylphosphine)-palladium, ((MeOOCC≡CCOOMe)Pd(PPh$_3$)$_2$) [156].

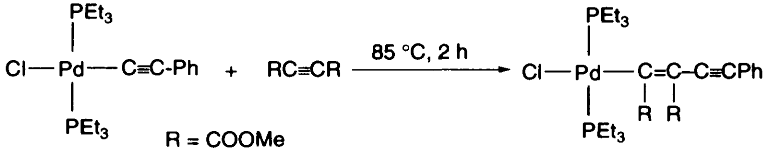


octahedral

Figure 20.3 Structure of fac-[Me$_3$Pd(bpy)I] [158]

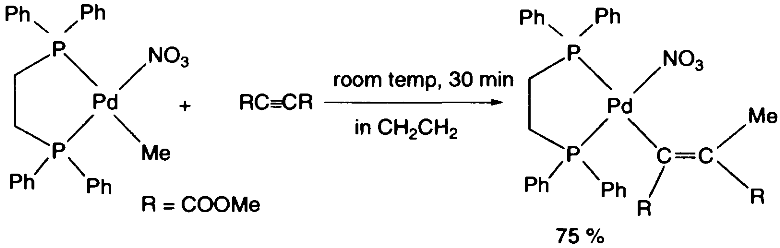
20.5.1 INSERTIONS

Organopalladium compounds are able to be inserted into Pd–C, Pd–O and Pd–N bonds by acetylene, olefins, isonitriles, SO_2, etc. as shown in eqs. (20.41)–(20.48) [159–174]. The activation barrier of insertion on the model of insertion to the Pd–CH_3 bond of $CH_3(CH{\equiv}CH)Pd(Cl)(NH_3)$ is calculated as 17 kcal/mol [169].

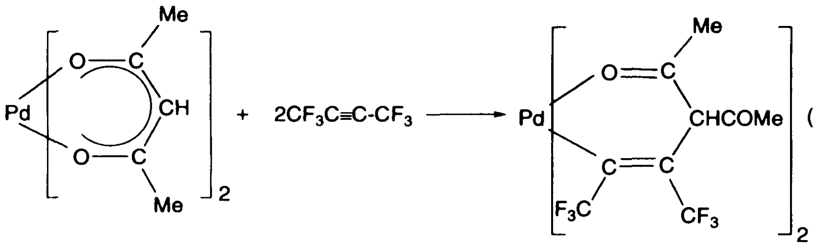


$$\mathrm{Cl{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}C{\equiv}C{-}Ph} + \mathrm{RC{\equiv}CR} \xrightarrow{85\ ^\circ\mathrm{C},\ 2\ \mathrm{h}} \mathrm{Cl{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}\underset{R}{C}{=}\underset{R}{C}{-}C{\equiv}CPh} \qquad \mathrm{R = COOMe}$$

(20.41)



(20.42)



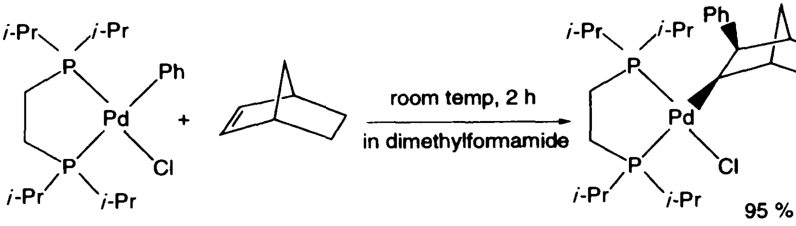
(20.43)

$$\mathrm{PhPdNHPh(PMe_3)_2} + \mathrm{CO_2} \xrightarrow[\text{in pentane}]{\text{room temp, 12 h}} \underset{81.6\ \%}{\mathrm{PhPd{-}OCONHPh(PMe_3)_2}} \qquad (20.44)$$

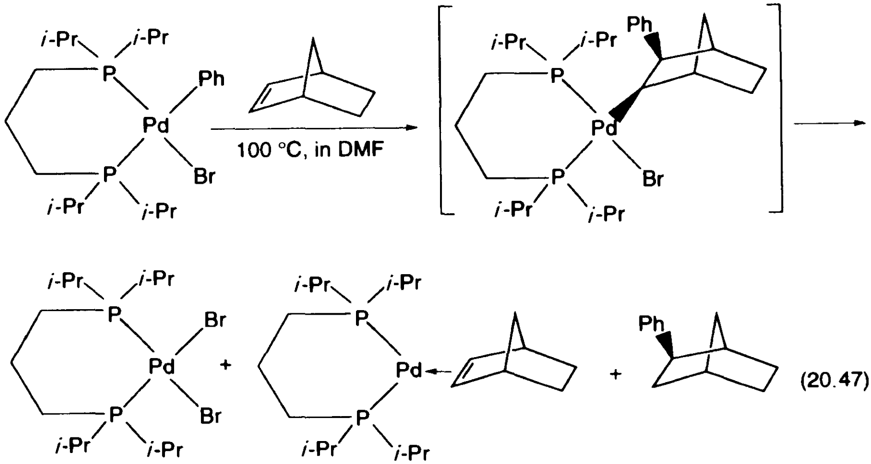
$$\mathrm{CpRPdPPh_3} + \mathrm{SO_2} \xrightarrow[\text{in benzene}]{25\ ^\circ\mathrm{C}} \mathrm{Cp(PPh_3)Pd{-}SO_2{-}R} \qquad (20.45)$$

R = Me, Ph

As shown in eq. (20.46) norbornene inserts almost quantitatively to Pd–Ph bond. But, in the similar reaction at elevated temperature, the decomposition products containing π-complex of norbornene are formed as shown in eq. (20.47) [170].

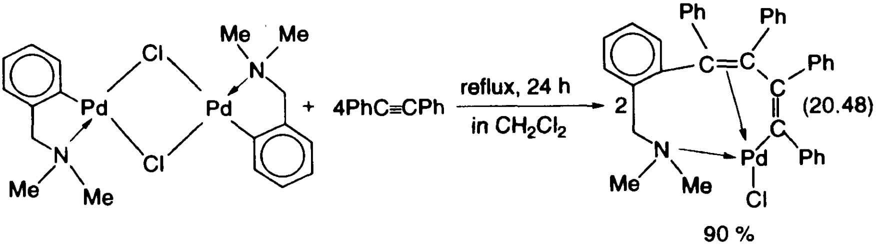


(20.46)



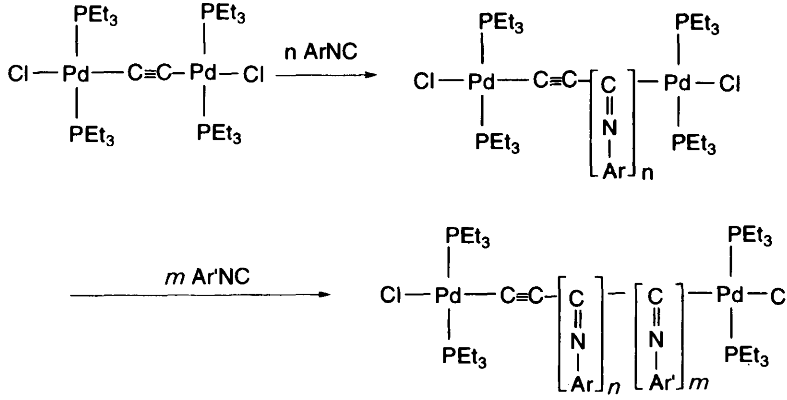
(20.47)

N,N-Dimethylaminobenzene complexes obtained by cyclometalations are stable five-membered ring compounds. But the insertion of diphenylacetylene proceeds to give ring expansion products by the insertion of two molecules as shown in eq. (20.48) [171].



(20.48)

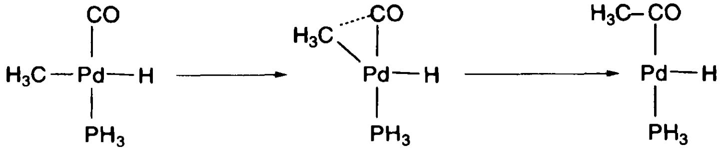
Isonitrile is liable to insertion to form high molecular weight polymers by a living polymerization as shown in eq. (20.49) [167].



(20.49)

Ar, Ar' = Ph, p-C_6H_4-C_4H_9, p-C_6H_4-C_8H_{17}
$n = 10-100$, $m = 30-100$

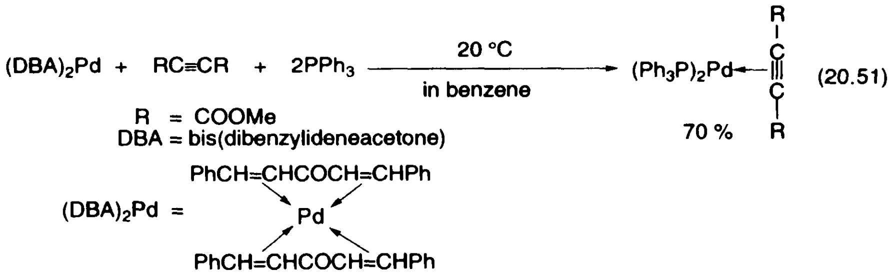
The reaction from Me-M-CO to M-$COCH_3$ is a methyl migration and not a carbonylation as shown in eq. (20.50). With Me(CO)Pd(PH_3)H it was proved that methyl migration proceeds via a three-center transition state by means of the *ab initio* MO method with the energy gradient as shown in eq. (20.50) [174]. Thus evidence of this reaction is also obtained by its similarity to the studies using $C^{13}O$ with organomagnesium compounds in Chapter 14.

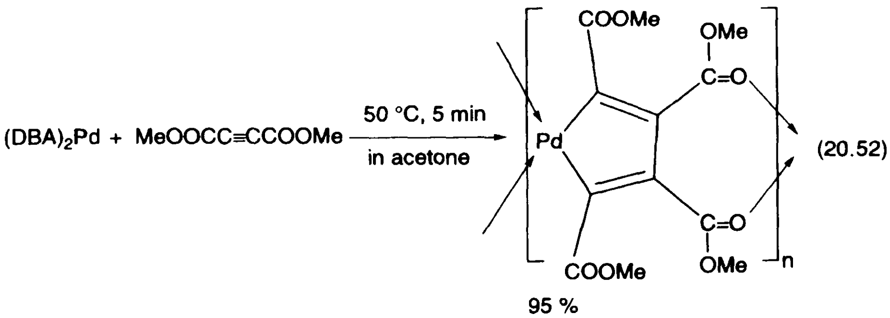


(20.50)

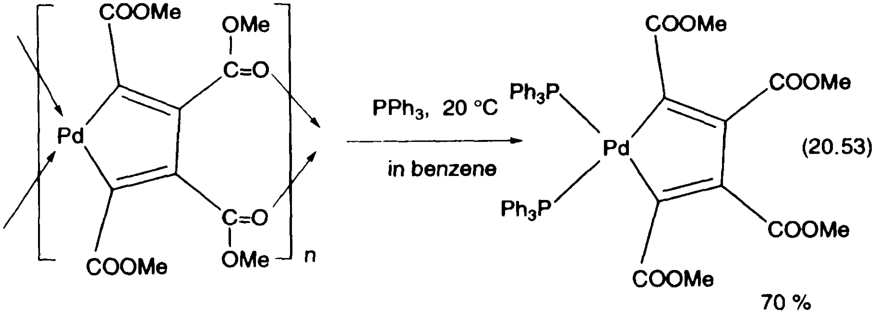
20.5.2 CYCLIC DIMERIZATIONS

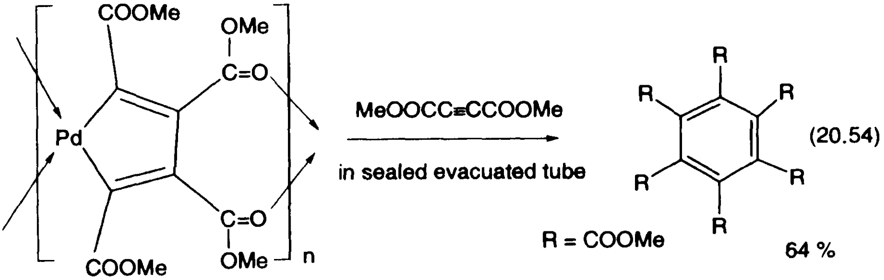
As bisbenzylideneacetonepalladium ($(DBA)_2Pd$) is stable similar to $(COD)_2Pd$, it is able to be used as the raw material for the synthesis of organopalladium compounds as shown in eq. (20.51). Reaction with acetylene compounds in the presence of phosphine affords an acetylene π-complex as shown in eq. (20.8). However, the reaction of these compounds by slight heating in the absence of phosphine affords a polymeric cyclic dimerization product as shown in eq. (20.52)





[147–154]. Further, the reaction with phosphine affords a cyclic dimerization product as shown in eq. (20.53). On the other hand, the reaction with another acetylene compound affords the benzene derivative as shown in eq. (20.54) [153].





20.6 ORGANIC SYNTHESES WITH PALLADIUM COMPOUNDS

Many articles, reviews and books on organic synthesis with palladium compounds have been published [1,2,175–210]. Palladium compounds are widely used and these reactions are variously classified. Recently, Tsuji arranged the reactions with palladium compounds into two sets of oxidative reactions with Pd(II) catalysts and various kinds of reactions with Pd(0) catalysts [1,2]. This book similarly classifies and shows their characteristics.

20.6.1 OXIDATIVE REACTIONS WITH Pd(II) CATALYSTS

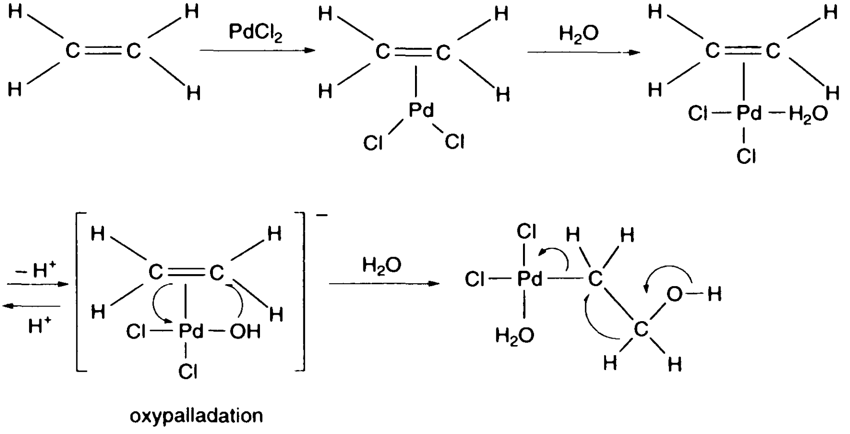
Pd(II) catalysts are usually $PdCl_2$, $Pd(OAc)_2$, $Pd(OCOCF_3)_2$, $PdCl_2(RCN)$, Li_2PdCl_4 and Na_2PdCl_4, etc. The reaction with Pd(II) catalysts proceeds oxidatively. The Pd(II) is reduced to Pd(0) in the reactions. Hence, for the reactions proceeding continuously with Pd(II) catalysts, the reaction requires the reoxidant which is able immediately to oxidize the Pd(0) formed in the reaction system. The reoxidants are $CuCl_2$, H_2O_2, t-BuOOH, $Cu(NO_3)_2$, $Cu(OAc)_2$ and benzoquinone. The oxidative reactions with Pd(II) catalysts are mainly as follows [1,2].

(1) Oxidative reactions of olefins
(2) Oxidative reactions of aromatic rings
(3) Oxidative carbonylations

20.6.1.1 Oxidative Reactions of Olefins

A representative reaction with palladium catalysts in the Wacker process. The Wacker process is the reaction in which ethylene is oxidized to acetaldehyde with Pd(II) catalysts such as $PdCl_2$. Palladium is liable to form a π-complex with unsaturated hydrocarbons such as olefins and acetylenes as described above. The Wacker process is thought to be as shown in Scheme 20.1 because palladium is liable to form the π-complex with carbon–carbon unsaturated compounds such as ethylene. Palladium is liable to form the square planar structure of four-coordination rather than three-coordination, and the carbons of ethylene bonded with palladium metal increase reactivity to a nucleophile such as water [175,204,206,210,211]. Pd(0) formed is converted to Pd(II) by a reoxidant $CuCl_2$. Then the catalysts are continuously reactivated. The Wacker process developed in 1958 is replaced by the Monsanto process (see Chapter 18) using a rhodium catalyst by 1980 [1,2].

$$CH_2{=}CH_2 \quad + \quad \tfrac{1}{2}O_2 \xrightarrow{\text{Pd(II), CuCl}_2} CH_3CHO \qquad (20.55)$$



$$\longrightarrow CH_3CHO + Pd(0) + HCl + Cl^- + H_2O$$

$$CH_2{=}CH_2 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd(0) + 2HCl$$

$$Pd(0) + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O$$

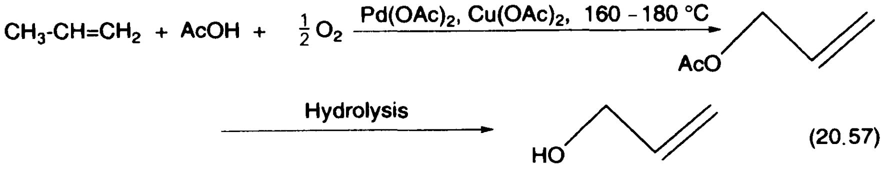
$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \longrightarrow CH_3CHO$$

Scheme 20.1 [175,204,205,210,211].

The production of vinylacetate by oxidative acetoxylation is one industrial process with ethylene and in the presence of a palladium catalyst as shown in eq. (20.56) [206].

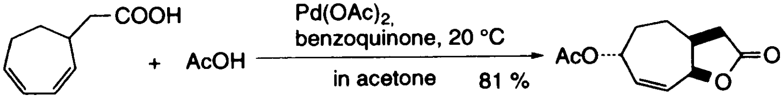
$$CH_2{=}CH_2 + AcOH + \tfrac{1}{2}O_2 \xrightarrow{Pd(OAc)_2,\ Cu(OAc)_2} CH_2{=}CHOAc + H_2O \quad (20.56)$$

The Showa Denko process is the oxidative acetoxylation of propylene as shown in eq. (20.57). The allylacetate produced is hydrolyzed to yield allylalcohol. The allylalcohol is used as a raw material for epichlorohydrin, glycerol and 1,4-butanediol.



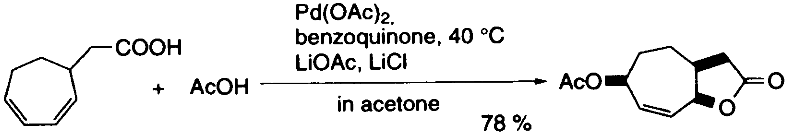
(20.57)

Reactions with benzoquinone as the reoxidant are shown in eqs. (20.58) and (20.59). Acetoxylactonization products are prepared stereoselectively according to the reaction conditions [192].



(20.58)

>98% 1α, 4β, 5β

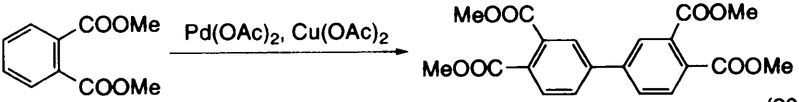


(20.59)

>98% 1β, 4β, 5β

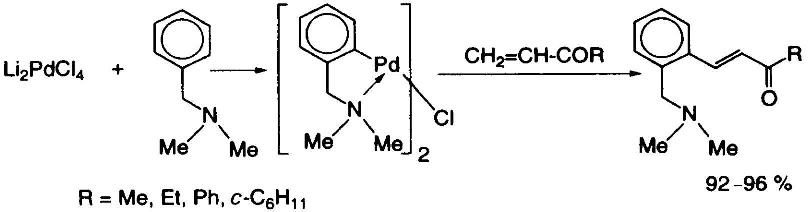
20.6.1.2 Oxidative Reactions of Aromatic Compounds

$PdCl_2$ as catalyst for the oxidative reactions of aromatic compounds has a low reactivity, so usually $Pd(OAc)_2$ is used. For example, as shown in eq. (20.60), the oxidative coupling reaction of phthalic acid diester proceeds to afford a tetracarboxylic acid derivative [2]. The tetracarboxylic acid is industrially used as a monomer of polyimide.



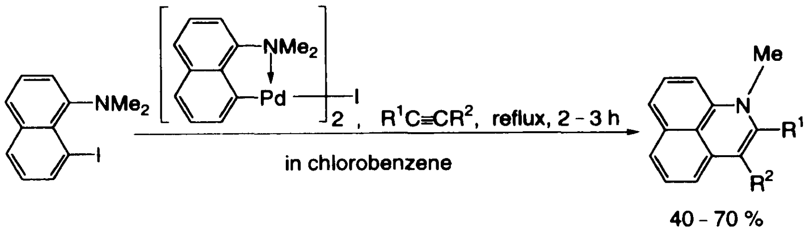
(20.60)

Cyclometalations proceed as shown in eqs. (20.35)–(20.39). With palladium compounds, these reactions are called cyclopalladation or orthopalladation. As the palladium bonded to an aromatic ring is very reactive, alkenes, alkynes, CO and halogen are easily replaced. For example, as shown in eq. (20.61), ortho-aryl derivatives are selectively prepared in high yield [212].



(20.61)

Cyclopalladation products react with alkynes to be inserted into the palladium–carbon bond, followed by reductive elimination of Pd(0), which leads to the formation of a C–N bond. Then the heterocyclic compound is yielded as shown in eq. (20.62) [195,213].

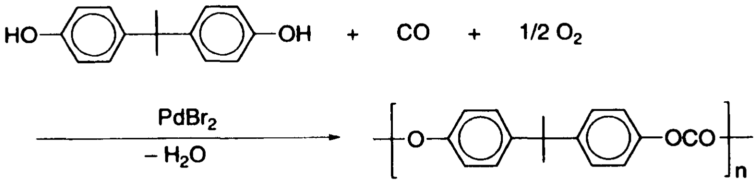


(20.62)

R^1 = Ph, COOMe, CF_3, R^2 = Ph, 4-$NO_2C_6H_4$, Me, Et, etc.

20.6.1.3 Oxidative Carbonylations

The preparation of polycarbonate by the carbonylation of bisphenol-A is one of oxidative carbonylation as shown in eq. (20.63) [2,214,215]. Preferably, the catalyst is $PbBr_2$, the reoxidant is $Mn(acac)_2$ and the solvent is methylene chloride. The process attracts attention as a polymerization process without using toxic phosgene.



(20.63)

20.6.2 REACTIONS WITH Pd(0) CATALYSTS

Pd(0) catalysts do not require the reoxidant by which Pd(0) formed is oxidized back to Pd(II). The Pd(0) catalysts are usually used as supporting palladium on a minute carbon surface, e.g., Pd/C or the phosphine catalysts, e.g., $Pd(PPh_3)_4$. In the latter case, $Pd(PPh_3)_4$ or a mixture of $Pd(OAc)_2$ and PPh_3 which form a phosphine palladium complex in the reaction system, are used. Halides or compounds which are liable to form a π-complex are used as substrates in the reaction with the Pd(0) catalyst.

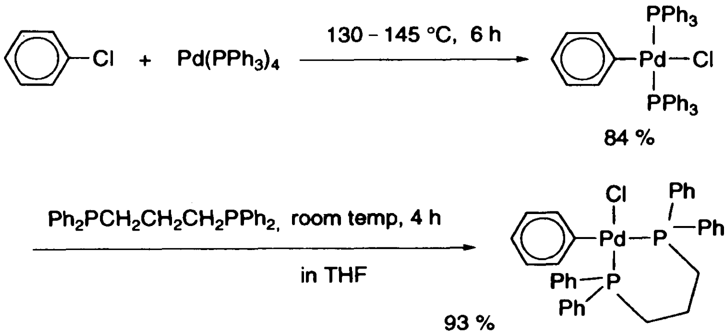
Reactions with Pd(0) catalysts are as follows.

(1) Reactions with aryl halides

(2) Reactions of allyl compounds or conjugate dienes via π-allyl palladium compounds.
(3) Carbonylations and others

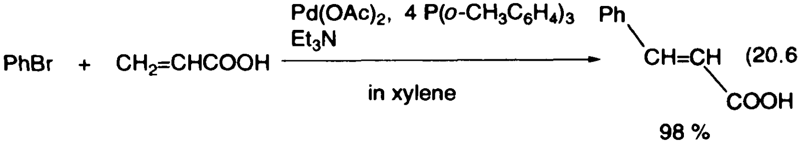
20.6.2.1 Reactions with Aryl Halides

Aromatic halides are low reactivity compounds in usual organic chemistry, but they are reactive to transition elements such as palladium. Therefore, palladium compounds are able to be added oxidatively by low reactivity chlorine of halides as shown in eq. (20.64). Further, diphosphine reacts with an oxidative addition product to afford a chelate compound. Its structure was determined by X-ray diffraction studies [216].



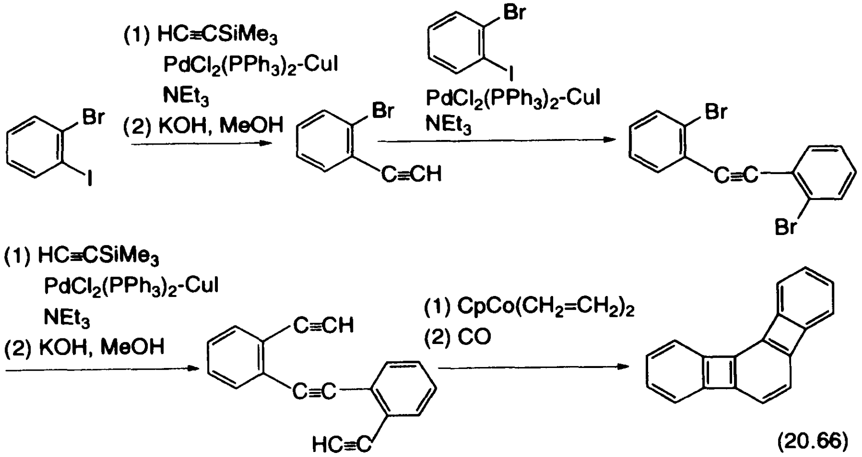
(20.64)

As shown in eqs. (20.1)–(20.6), palladium compounds have a high reactivity to alkenyl compounds. Aryl palladium compounds easily afford alkenyl reaction products in the presence of a base as shown in Scheme 20.2. Thus the reaction is called Heck arylation [217–219]. For example, bromobenzene reacts with acrylic acid to afford (E)PhCH=CHCOOH almost quantitatively as shown in eq. (20.65) [218]. The Heck reactions are applied for the synthesis of polycyclic compounds or polymerization as shown in eqs. (20.66) and (20.67) [201,220].

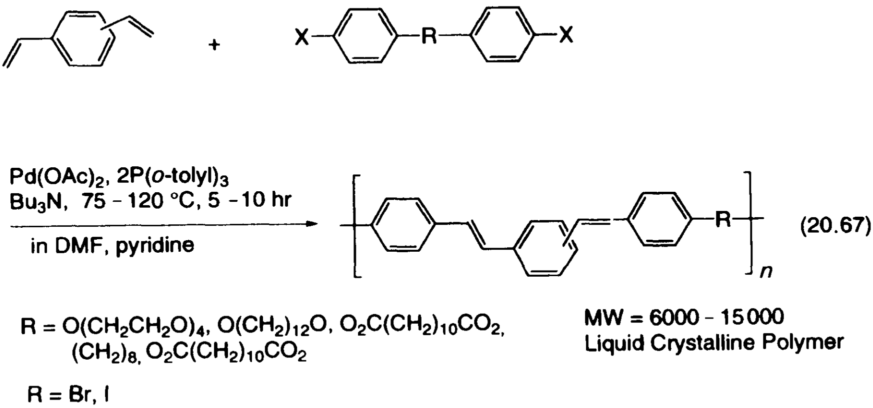


$$\mathrm{PhBr} + \mathrm{CH_2{=}CHCOOH} \xrightarrow[\text{in xylene}]{\mathrm{Pd(OAc)_2},\ 4\ \mathrm{P}(o\text{-}\mathrm{CH_3C_6H_4})_3,\ \mathrm{Et_3N}} \mathrm{Ph{-}CH{=}CH{-}COOH} \quad (20.65)$$

98 %

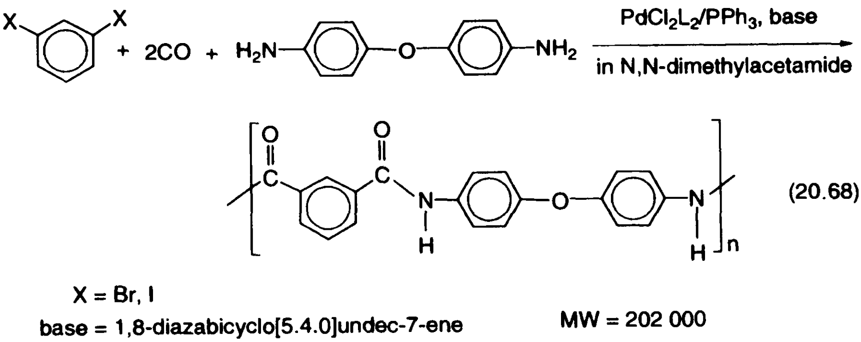


(20.66)

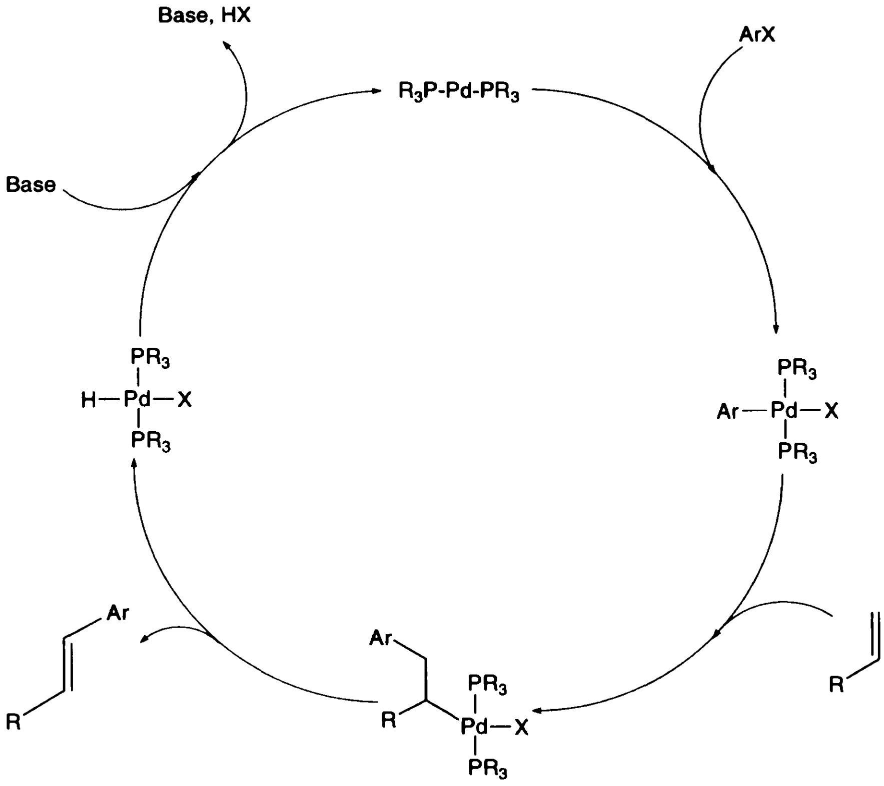


(20.67)

The further example of polymerization with Pd(0) catalysts by carbonylation is shown in eq. (20.68) [197].

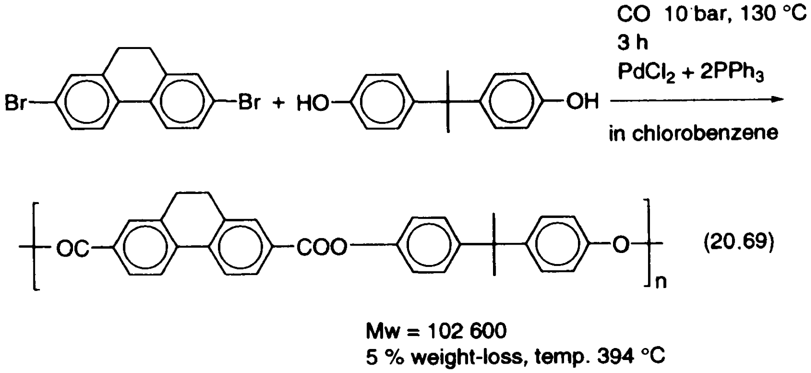


(20.68)



Scheme 20.2 [219–221].

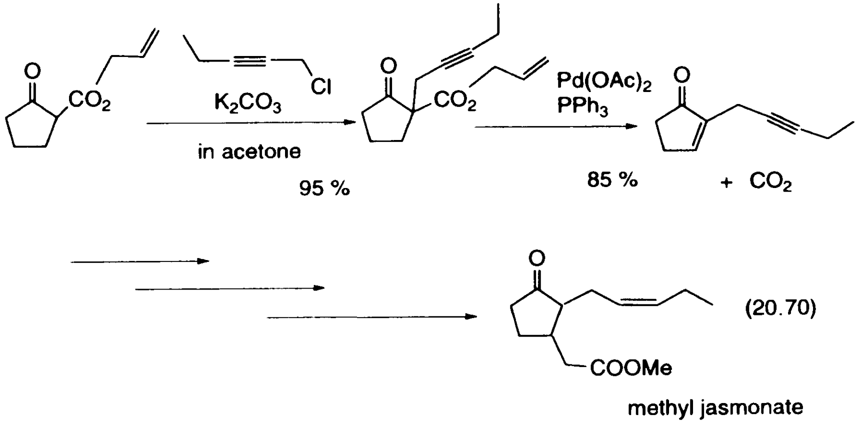
Recently, highly polymeric polyesters are prepared by the reaction of biphenyldibromide with a diol as shown in eq. (20.69) [220a].



(20.69)

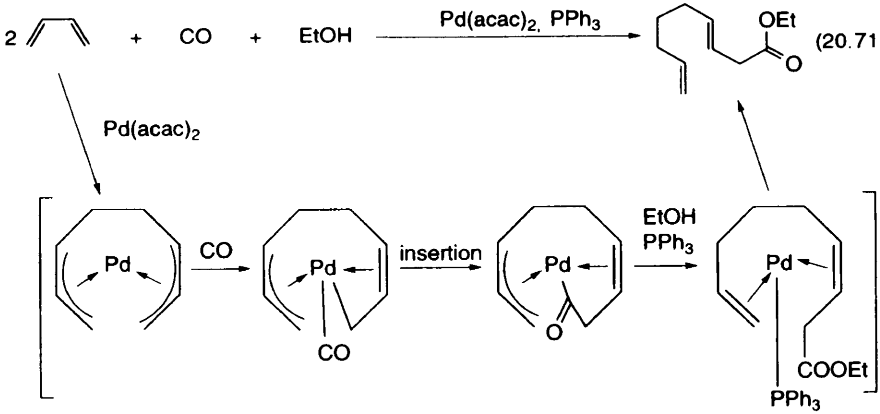
20.6.2.2 Reactions of Allyl Compounds or Conjugate Diene Compounds via π-Allyl Compounds

Allyl compounds or conjugate dienes are liable to form π-allyl complexes. For example, as shown in eq. (20.70), decarboxylation and dehydrogenation proceed via π-allyl complexes to afford the intermediate of methyl jasmonate used for perfume [1,2,177,178,221,222].



(20.70)

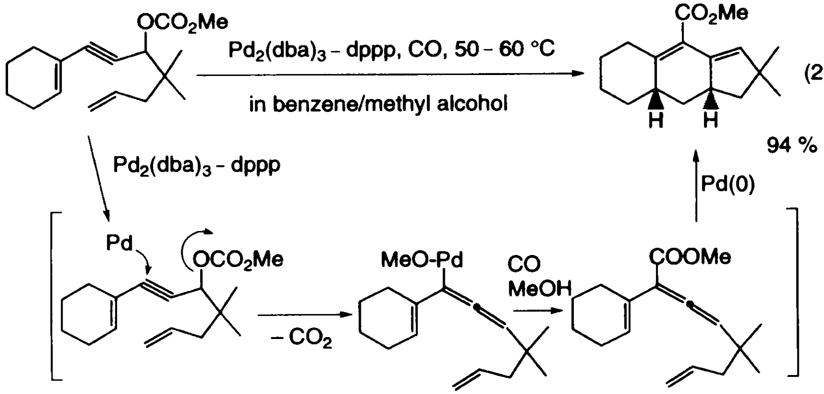
Butadiene reacts in the presence of Pd(0) catalyst to afford the dimer easily and in the presence of carbon monoxide and alcohol to afford the esters as shown in eq. (20.71) [223].



(20.71)

20.6.2.3 Carbonylations and Others

As shown in eq. (20.72), in the presence of a compound having a double bond or triple bond, a five- or six-membered ring compound is formed by carbonylation and cyclization via a palladium complex [13].

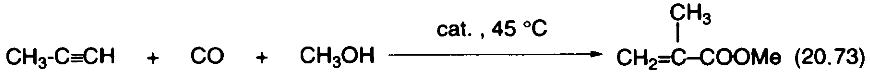


(20.72)

dppp = 1,3-bis(diphenylphosphino)propane
= $Ph_2P\text{-}CH_2CH_2CH_2\text{-}PPh_2$

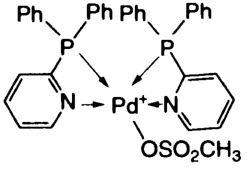
Many other cyclization reactions with palladium catalysts have been reported [188,224–227].

Recently, in the Shell Institute, as shown in eq. (20.73), the production process of metacrylic acid has been developed with a diphenylphosphinepyridium palladium complex cationic catalyst. The turnover number (mol/mol Pd h) is 40 000 or more [228,229].



$$CH_3\text{-}C{\equiv}CH \;+\; CO \;+\; CH_3OH \xrightarrow{\text{cat.}\,,\,45\ ^\circ C} CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}\text{—}COOMe \qquad (20.73)$$

cat. =



average reaction rate = 40 000 mol/mol Pd hr
methyl methacrylate selectivity >99.95 %

$CH_3SO_3^-$

REFERENCES

[1] J. Tsuji, *Shokubai*, **31** (1989) 262.
[2] J. Tsuji, *Synthesis*, (1990) 739.
[3] J. Tsuji, *Palladium Reagents and Catalysts*, John Wiley, Chichester, 1996.
[4] J. Tsuji, *Organic Synthesis with Palladium Compounds*, Springer-Verlag, Berlin, 1980.
[5] *Kagaku Daijiten*, Tokyo Kagaku Doojin, Tokyo, p. 1798, 1989.
[6] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
[7] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., John Wiley, New York, vol.18, p. 228, 1980.
[8] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, 4th ed., p. 997, 1987.
[9] *Sekai Dai Hyakkajiten*, Heibonsha, Tokyo, vol.23, p. 50, 1988.
[10] *Sekai Kagaku Daijiten, Technopia (Encyclopedia of Science and Technology)*, Kodansha, Tokyo, vol.14, p. 384, 1977.
[11] P.M. Maitlis, P. Espinet and M.J.H. Russell, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel eds., Pergamon Press, Oxford, vol.6, p. 233, 1982.
[12] *Jikken Kagaku Kouza 18, 4th ed., Yuki Kinzoku Sakutai*, Japan Chem. Soc. ed., Maruzen, Tokyo, p. 391, 1991.
[13] I. Yamamoto ed., *Yuki Kinzoku Kagoubutsu, Goseiho oyobi Riyouhou*, Tokyo Kagaku Dojin, Tokyo, p. 225, 1991.
[14] A. Visser, R. van der Linde and R.O. De Jongh, *Inorg. Syntheses*, **16** (1974) 127.
[15] S. Takahashi and N. Hagihara, *Nihon Kagaku Zasshi*, **88** (1967) 1306.
[16] D. Drew and J.R. Doyle, *Inorg. Synthesis*, **13** (1972) 47.
[17] J. Chatt, L.M. Vallarino and L.M. Venanzi, *J. Chem. Soc.*, (1957) 3413.
[18] J. Smidt and W. Hafner, *Angew. Chem.*, **71** (1959) 284.
[19] W.T. Dent, R. Long and A.J. Wilkinson, *J. Chem. Soc.*, (1964)1585.
[20] J.K. Nicholson, J. Powell and B.L. Shaw, *J. Chem. Soc. Chem. Commun.*, (1966)174.
[21] H.C. Volger, *Rec. Trav. Chim.*, **87** (1968) 225.
[22] R.J. Cross and R. Wardle, *J. Chem. Soc. A*, (1971) 2000.
[23] E.O. Greaves and P.M. Maitlis, *J. Organomet. Chem.*, **6** (1966) 104.
[24] E.O. Greaves, C.J.L. Lock and P.M. Maitlis, *Can. J. Chem.*, **46** (1968) 3879.
[25] V.V. Bashilov, P.V. Petrovskii, V.I. Sokolov, S.V. Lindeman, I.A. Guzey and Y.T. Struchkov, *Organometallics*, **12** (1993) 991.
[26] J. Powell and B.K. Shaw, *J. Chem. Soc. A*, (1968) 774.
[27] M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, *J. Chem. Soc. Dalton Trans.*, (1977) 271.
[28] T. Ito, S. Hasegawa, Y. Takahashi and Y. Ishii, *J. Organomet. Chem.*, **73** (1974) 401.
[29] M. Donati and F. Conti, *Tetrahedron Lett.*, (1966) 1219.
[30] M. Sakamoto, I. Shimizu and A. Yamamoto, *Organometallics*, **13** (1994) 407.
[31] Y. Takahashi, T. Ito, S. Sakai and Y. Ishii, *J. Chem. Soc. Chem. Commun.*, (1970)1065.
[32] G. Calvin and G.E. Coates, *J. Chem. Soc.*, (1960)2008.
[33] C.J. Moulton and B.L. Shaw, *J. Chem. Soc. Dalton Trans.*, (1976)1020.
[34] T. Ito, H. Tsuchiya and A. Yamamoto, *Bull. Chem. Soc. Japan*, **50** (1977) 1319.
[35] J.K. Becconsall, G.E. Job and S. O'Brien, *J. Chem. Soc. A*, (1967)423.
[36] F. Morandini, G. Consiglio and F. Wenzinger, *Helv. Chim. Acta*, **62** (1979) 59.
[37] A. Misono, Y. Uchida, M. Hidai and K. Kudo, *J. Organomet. Chem.*, **20** (1969) P7.
[38] K. Kudo, M. Hidai and Y. Uchida, *J. Organomet. Chem.*, **33** (1971) 393.

[39] C. Wang, H. Willner, M. Bodenbinder, R.J. Batchelor, F.W.B. Einstein and F. Aubke, *Inorg. Chem.*, **33** (1994) 3521.

[40] P. Veya, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, **12** (1993) 4899.

[41] M. Onishi, H. Yamamoto and K. Hiraki, *Bull Chem. Soc. Japan*, **51** (1978) 1856.

[42] P. Fitton and J.E. McKeon, *J. Chem. Soc. Chem. Commun.*, (1968)4.

[43] P. Fitton, M.P. Johnson and J.E. McKeon, *J. Chem. Soc. Chem. Commun.*, (1968) 6.

[44] K.J. Klabunde, J.Y.E. Low and H.F. Efner, *J. Am. Chem. Soc.*, **96** (1974) 1984.

[45] K.J. Klabunde and J.Y.F. Low, *J. Organomet. Chem.*, **51** (1973) C33.

[46] R.D. Rieke and A.V. Kavaliunas, *J. Org. Chem.*, **44** (1979) 3069.

[47] K.J. Klabunde and J.Y.F. Low, *J. Am. Chem. Soc.*, **96** (1974) 7674.

[48] R.D. Rieke, W.J. Wolf, N. Kujundzic and A.V. Kavaliunas, *J. Am. Chem. Soc.*, **99** (1977) 4159.

[49] B. Crociani, T. Boschi and U. Belluco, *Inorg. Chem.*, **9** (1970) 2021.

[50] S. Otsuka, A. Nakamura and T. Yoshida, *J. Am. Chem. Soc.*, **91** (1969) 7196.

[51] S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto and K. Ataka, *J. Am. Chem. Soc.*, **95** (1973) 3180.

[52] W.P. Fehlhammer, A. Mayr and B. Olegemöller, *Angew. Chem.*, **87** (1975) 290.

[53] E.O. Fischer and H. Werner, *Chem. Ber.*, **95** (1962) 703.

[54] J.R. Doyle, P.E. Slade and H.B. Jonassen, *Inorg. Syntheses*, **6** (1960) 216.

[55] Y. Yamamoto and H. Yamazaki, *Bull Chem. Soc. Japan*, **58** (1985) 1843.

[56] S. Otsuka, A. Nakamura and Y. Tatsuno, *J. Am. Chem. Soc.*, **91** (1969) 6994.

[57] M.F. Rettig, E.A. Kirk and P.M. Maitlis, *J. Organomet. Chem.*, **111** (1976) 113.

[58] I. Omae, *Organometallic Intramolecular-coordination Compounds*, *J. Organometallic Chemistry Library 18*, Elsevier, Amsterdam, 1986.

[59] I.P. Parkin, J.D. Woollins and P.S. Belton, *J. Chem. Soc. Dalton Trans.*, (1990) 511.

[60] P. Espinet, G. García, G.J. Herrero, Y. Jeannin and M. Philoche-Levisalles, *Inorg. Chem.*, **28** (1989) 4207.

[61] J. Granell, R. Moragas, J. Sales, M. Font-Bardía and X. Solans, *J. Chem. Soc. Dalton Trans.*, (1993)1237.

[62] A. Crispini, G. DeMunno, M. Ghedini and F. Neve, *J. Organomet. Chem.*, **427** (1992) 409.

[63] P.W. Clark, S.F. Dyke, G. Smith and C.H.L. Kennard, *J. Organomet. Chem.*, **330** (1987) 447.

[64] J. Granell, R. Moragas, J. Sales, M. Font-Bardía and X. Solans, *J. Organomet. Chem.*, **431** (1992) 359.

[65] J.M. Vila, M. Gayoso, A. Fernandez, N.A. Bailey and H. Adams, *J. Organomet. Chem.*, **448** (1993) 223.

[66] J. Barro, J. Granell, D. Sainz, J. Sales, M. Font-Bardía and X. Soland, *J. Organomet. Chem.*, **456** (1993) 147.

[67] C. Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J.H. Rodriguez, J.R. Masaguer and J.L. García-Ruano, *J. Organomet. Chem.*, **476** (1994) 19.

[68] C. López, X. Solans and D. Tramuns, *J. Organomet. Chem.*, **471** (1994) 265.

[69] J.M. Vila, M. Gayoso, J.J. Fernandez, J.M. Ortigueira, A. Fernandez, N.A. Bailey and H. Adams, *J. Organomet. Chem.*, **471** (1994) 259.

[70] J.M. Vila, M. Gayoso, T. Pereira, C. Rodríguez, J.M. Ortigueira, J.J. Fernández and J.L. Torres, *J. Organomet. Chem.*, **479** (1994) 37.

[71] J.L. García-Ruano, I. López-Solera, J.R. Masaguer, M.A. Monge, C. Navarro-Ranninger and J.H. Rodríguez, *J. Organomet. Chem.*, **476** (1994) 111.

[72] M.J. Baena, J. Buey, P. Espinet, H.-S. Kitzerow and G. Heppke, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 1201.

[73] L.A. Villanueva, K.A. Abboud and J.M. Bonceila, *Organometallics*, **13** (1994) 3921.

[74] R. Bosque, C. López, J. Sales, X. Solans and M. Font-Bardía, *J. Chem. Soc. Dalton Trans.*, (1994) 735.

[75] M.C. Navarro-Ranninger, A. Alvarez-Valdés, M.J. Camazón, J. Román and R. Lozano, *J. Organomet. Chem.*, **331** (1978) 107.

[76] J. Albert, J. Granell, J. Sales, X. Solans and M. Font-Altaba, *Organometallics*, (1986) 2567.

[77] J.M. Vila, M.T. Pereira, E. Gayoso and M. Gayoso, *Transition Met. Chem.*, **11** (1986) 342.

[78] J. Granell, D. Sainz, J. Sales, X. Solans and M. Font-Altaba, *J. Chem. Soc. Dalton Trans.*, (1986) 1785.

[79] J.M. Vila, M. Gayoso, M.T. Pereira, A. Romar, J.J. Fernández and M. Thornton-Pett, *J. Organomet. Chem.*, **401** (1991) 385.

[80] R. Bosque, J. Granell, J. Sales, M. Font-Bardía and X. Solans, *J. Organomet. Chem.*, **453** (1993) 147.

[81] M.J. Baena, P. Espinet, M.B. Ros, J.S. Serrano and A. Ezcurra, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 1203.

[82] J. Vicente, J.A. Abad, J. Gil-Rbio, P.G. Jones and E. Bernbenek, *Organometallics*, **12** (1993) 4151.

[83] S.A. Hudson and P.M. Maitlis, *Chem. Rev.*, **93** (1993) 861.

[84] C. López, R. Bosque, X. Solans, M. Font-Bardía, J. Silver and G. Fern, *J. Chem. Soc. Dalton Trans.*, (1995) 1839.

[85] M.J. Baena, J. Barberá, P. Espinet, A. Ezcurra, M.B. Ross and J.L. Serrano, *J. Am. Chem. Soc.*, **116** (1994) 1899.

[86] A.C. Cope and R.W. Siekman, *J. Am. Chem. Soc.*, **87** (1965) 3272.

[87] A. Crispini, M. Ghedini and F. Neve, *J. Organomet. Chem.*, **448** (1993) 241.

[88] S. Armentano, A. Crispini, G. De Munno, M. Ghedini and F. Neve, *Acta Cryst.*, **C47** (1991) 966.

[89] J. Vicente, M.-D. Bermuúdez, M.-T. Chinote and J.-J. Sanchez-Santano, *J. Chem. Soc. Chem. Commun.*, (1989) 141.

[90] G. Wu, A.L. Rheingold and R.F. Heck, *Organometallics*, **6** (1987) 2386.

[91] G.K. Anderson and R.J. Cross, *J. Chem. Soc. Chem. Commun.*, (1986)1502.

[92] G. Wu, A.L. Rheingold and R.F. Heck, *Organometallics*, **5** (1986) 1922.

[93] S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, (1986) 3765.

[94] M. Ghedini, S. Armentano, F. Neve and S. Licoccia, *J. Chem. Soc. Dalton Trans.*, (1988) 1565.

[95] C. Sinha, D. Bandyopadhyay and A. Chakravorty, *Inorg. Chem.*, **27** (1988) 1173.

[96] T. Janecki, J.A.D. Jeffreys, P.L. Pauson, A. Pietrzykowski and K.J. McCullough, *Organometallics*, **6** (1987) 1553.

[97] M. Ghedini, S. Armentano and F. Neve, *Inorg. Chim. Acta*, **134** (1987) 23.

[98] A.C. Cope and E.C. Friedrich, *J. Am. Chem. Soc.*, **90** (1968) 909.

[99] K. Tani, H. Tashiro, M. Yoshida and T. Yamagata, *J. Organomet. Chem.*, **469** (1994) 229.

[100] N. Gabbitas, G. Salem, M. Sterns and A.C. Willis, *J. Chem. Soc. Dalton Trans.*, (1993)3271.

[101] P.L. Alsters, J. Boersma and G. van Koten, *Organometallics*, **12** (1993) 1629.

[102] P.L. Alsters, P.F. Engel, M.P. Hogerheide, M. Copijn, A.L. Spek and G. van Koten, *Organometallics*, **12** (1993) 1831.

[103] J.-M. Valk, F. Maassarani, P. van der Sluis, A.L. Spek, J. Boersma and G. van Koten, *Organometallics*, **13** (1994) 2320.

[104] F. Balegroune, P. Craunstein, T.M.G. Carneiro, D. Grandjean and D. Matt, *J. Chem. Soc. Chem. Commun.*, (1989) 582.

[105] G. van Koten, *Pure Appl. Chem.*, **61** (1989) 1681.

[106] P. Braunstein, D. Matt, D. Nobel and J. Fischer, *J. Chem. Soc. Chem. Commun.*, (1987) 1530.

[107] S.-E. Bouaound, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, **27** (1988) 2279.

[108] A.D. Ryabov, *Inorg. Chem.*, **26** (1987) 1252.

[109] J. Terheijden, G. van Koten, D.M. Grove, K. Vrieze and A.L. Spek, *J. Chem. Soc. Dalton Trans.*, (1987) 1359.

[110] F. Maassarani, M. Pfeffer, G. Le Borgne, J.T.B.H. Jastrzebski and G. van Koten, *Organometallics*, **6** (1987) 1111.

[111] A.J. Deeming, M.N. Meah, P.A. Bates and M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, (1988) 2193.

[112] L. Dai, Z. Zhou, Y. Zhang, C. Ni, Z. Zhang and Y. Zhou, *J. Chem. Soc. Chem. Commun.*, (1987) 1760.

[113] G. Wu, A.L. Rheingold, S.J. Geib and R.F. Heck, *Organometallics*, **6** (1987) 1941.

[114] P.G. Kerr, P.-H. Leung and S.B. Wild, *J. Am. Chem. Soc.*, **109** (1987) 4321.

[115] S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *J. Chem. Soc. Chem. Commun.*, (1987)488.

[115a] J. Vicente, I. Saura-Llamas and P.G. Jones, *J. Chem. Soc. Dalton Trans.*, (1993) 3619.

[115b] R.J. Doyle, G. Salem and A.C. Willis, *J. Chem. Soc. Dalton Trans.*, (1995) 1867.

[115c] P.L. Alsters, P.J. Baesjou, M.D. Janssen, H. Kooijman, A. Sicherer-Roetman, A.L. Speck and G. van Koten, *Organometallics*, **11** (1992) 4124.

[116] E. Wehman, G. van Koten, J.T.B.H. Jastrzebski, H. Ossor and M. Pfeffer, *J. Chem. Soc. Dalton Trans.*, (1988) 2975.

[117] P.H. Leung, A.C. Willis and S.B. Wild, *Inorg. Chem.*, **31** (1992) 1406.

[118] S.Y.M. Chooi, T.S.A. Hor, P.-H. Leung and K.F. Mok, *Inorg. Chem.*, **31** (1992) 1494.

[119] P.H. Leung, G.M. McLaughlin, J.W.L. Martin and S.B. Wild, *Inorg. Chem.*, **25** (1986) 3392.

[120] M. Pfeffer, N. Sutter-Beydoun, A. De Cian and J. Fischer, *J. Organomet. Chem.*, **453** (1993) 139.

[121] S.Y.M. Chooi, M.K. Tan, P.-H. Leung and K.F. Mok, *Inorg. Chem.*, **33** (1994) 3096.

[122] J.-M. Valk, R. van Belzen, J. Boersma, A.L. Spek and G. van Koten, *J. Chem. Soc. Dalton Trans.*, (1994) 2293.

[122a] M. Pabel, A.C. Willis and S.B. Wild, *Angew. Chem. Int. Ed. Engl.*, **33** (1994) 1835.

[122b] J. Leitch, G. Salem and D.C.R. Hockless, *J. Chem. Soc. Dalton Trans.*, (1995) 649.

[122c] J.-M. Valk, J. Boersma and G. van Koten, *J. Organomet. Chem.*, **483** (1994) 213.

[123] J. Ruiz, N. Cutillas, J. Torregrosa, G. García, G. López, P.A. Chaloner, P.B. Hitchcock and R.M. Harrison, *J. Chem. Soc. Dalton Trans.*, (1994) 2353.

[124] J. Forniés, R. Navarro, V. Sicilia and M. Tomás, *Organometallics*, **9** (1990) 2423.

[125] F. Maassarani, M. Pfeffer and G. Le Borgne, *Organometallics*, **6** (1987) 2029.

[126] F. Maassarani, M. Pfeffer and G. Le Borgne, *J. Chem. Soc. Chem. Commun.*, (1987) 565.

[127] G.R. Newkome and D.W. Evans, *Organometallics*, **6** (1987) 2592.

[127a] A. Yoneda, T. Hakushi, G.R. Newkome and F.R. Fronczek, *Organometallics*, **13** (1994) 4912.

[127b] S.Q. Huo, Y.J. Wu, C.X. Du, Y. Zhu, H.Z. Yuan and X.A. Mao, *J. Organomet. Chem.*, **483** (1994) 139.

[128] J.C. Gaunt and B.L. Shaw, *J. Organomet. Chem.*, **102** (1975) 511.

[129] C. López, R. Bosque, X. Solans, M. Font-Bardía, D. Tramuns, G. Fern and J. Silver, *J. Chem. Soc. Dalton Trans.*, (1994) 3039.

[130] J. Dupont, N. Beydoun and M. Pfeffer, *J. Chem. Soc. Dalton Trans.*, (1989) 1715.

[131] J. Dupont, M. Pfeffer, J.C. Daran and Y. Jeannin, *Organometallics*, **6** (1987) 899.

[132] J. Dupont and M. Pfeffer, *J. Chem. Soc. Dalton Trans.*, (1990) 3193.

[133] J.E. Kickham, S.J. Loeb and S.L. Murphy, *J. Am. Chem. Soc.*, **115** (1993) 7031.

[133a] H.-P. Abicht, *J. Organomet. Chem.*, **311** (1986) 57.

[134] M.A. Bennett and P.N. Kapoor, *J. Organomet. Chem.*, **336** (1987) 257.

[135] A.A. Watson, D.A. House and P.J. Steel, *J. Organomet. Chem.*, **311** (1986) 387.

[136] G. García-Herbosa, A. Muñoz, D. Miguel and S. García-Granda, *Organometallics*, **13** (1994) 1775.

[137] D.J. Cárdenas, A.M. Echavarren and A. Vegas, *Organometallics*, **13** (1994) 882.

[138] R.P. Thummel and Y. Jahng, *J. Org. Chem.*, **52** (1987) 73.

[139] A. Sen, *Acc. Chem. Res.*, **26** (1993) 303.

[140] Y. Yamamoto, T. Tanase, T. Yanai, T. Asano and K. Kobayashi, *J. Organomet. Chem.*, **456** (1993) 287.

[141] C.J. Moulton and B.L. Shaw, *J. Chem. Soc. Dalton Trans.*, (1976) 1020.

[142] R. McCrindle, G.J. Arsenault, R. Farwaha, A.J. McAlees and D.W. Sneddon, *J. Chem. Soc. Dalton Trans.*, (1989) 761.

[142a] C.A. Craig and R.J. Watts, *Inorg. Chem.*, **28** (1989) 309.

[142b] J. Albert, J. Granell, J. Sales, M. Font-Bardía and X. Solans, *Organometallics*, **14** (1995) 1393.

[142c] R. Bosque, C. López, J. Sales and X. Solans, *J. Organomet. Chem.*, **483** (1994) 61.

[142d] P.F. Engel, M. Pfeffer and J. Fischer, *Organometallics*, **13** (1994) 4751.

[142e] K. Hiraki, Y. Fuchita, M. Nakashima and H. Hiraki, *Bull. Chem. Soc. Japan*, **59** (1986) 3073.

[143] A.J. Cantry, N.J. Minchin, B.W. Skelton and A.H. White, *J. Chem. Soc. Dalton Trans.*, (1986) 2205.

[144] A.J. Canty, N.J. Minchin, B.W. Skelton and A.H. White, *J. Chem. Soc. Dalton Trans.*, (1987) 1477.

[145] F. Maassarani, M. Pfeffer and G. Le Borgne, *Organometallics*, **6** (1987) 2043.

[146] K. Sonogashira, T. Yatake, Y. Tohda, S. Takahashi and N. Hagihara, *J. Chem. Soc. Chem. Commun.*, (1977) 291.

[147] Y. Takahashi, T. Ito, S. Sakai and Y. Ishii, *J. Chem. Soc. Chem. Commun.*, (1970) 1065.

[148] K. Moseley and P.M. Maitlis, *J. Chem. Soc. Chem. Commun.*, (1971) 1604.

[149] T. Ito, Y. Takahashi and Y. Ishii, *J. Chem. Soc. Chem. Commun.*, (1972) 629.

[150] D.M. Roe, P.M. Bailey, K. Moseley and P.M. Maitlis, *J. Chem. Soc. Chem. Commun.*, (1972) 1273.

[151] K. Moseley and P.M. Maitlis, *J. Chem. Soc. Dalton Trans.*, (1974) 169.

[152] H. Suzuki, K. Itoh, Y. Ishii, K. Simon and J.A. Ibers, *J. Am. Chem. Soc.*, **98** (1976) 8494.

[153] L.D. Brown, K. Itoh, H. Suzuki, K. Hirai and J.A. Ibers, *J. Am. Chem. Soc.*, **100** (1978) 8232.

[154] T. Ito, S. Hasegawa, Y. Takahashi and Y. Ishii, *J. Organomet. Chem.*, **73** (1974) 401.

[155] A.L. Seligson and W.C. Trogler, *J. Am. Chem. Soc.*, **113** (1991) 2520.

[156] J.A. McGinnety, *J. Chem. Soc. Dalton Trans.*, (1974) 1038.

[157] P.K. Byers, A.J. Canty, B.W. Skelton and A.H. White, *J. Chem. Soc. Chem. Commun.*, (1986) 1722.

[158] A.J. Canty, *Acc. Chem. Res.*, **25** (1992) 83.

[159] Y. Tohda, K. Sonogashira and N. Hagihara, *J. Chem. Soc. Chem. Commun.*, (1975) 54.

[160] H.C. Clark, C.R.C. Milne and C.S. Wong, *J. Organomet. Chem.*, **136** (1977) 265.
[161] D.R. Russell and P.A. Tucker, *J. Chem. Soc. Dalton Trans.*, (1975) 1743.
[162] A.C. Jarvis, R.D.W. Kemmitt, B.Y. Kimura, D.R. Russell and P.A. Tucker, *J. Organomet. Chem.*, **66** (1974) C53.
[163] J.M. Boncella and L.A. Villanueva, *J. Organomet. Chem.*, **465** (1994) 297.
[164] G.K. Turner and H. Felkin, *J. Organomet. Chem.*, **121** (1976) C29.
[165] S. Otsuka, A. Nakamura and T. Yoshida, *J. Am. Chem. Soc.*, **91** (1969) 7196.
[166] J.F. van Baar, J.M. Klerks, P. Overbosch, D.J. Stufkens and K. Vrieze, *J. Organomet. Chem.*, **112** (1976) 95.
[167] K. Onitsuka, K. Yanai, F. Takei, T. Joh and S. Takahashi, *Organometallics*, **13** (1994) 3862.
[168] A.D. Ryabov, R. van Eldik, G. Le Borgne and M. Pfeffer, *Organometallics*, **12** (1993) 1386.
[169] P. de Vaal and A. Dedieu, *J. Organomet. Chem.*, **478** (1994) 121.
[170] M. Portnoy, Y. Ben-David, I. Rousso and D. Milstein, *Organometallics*, **13** (1994) 3465.
[171] A. Bahsoun, J. Dehand, M. Pfeffer, M. Zinsius, S.-E. Bouaoud and G. Le Borgne, *J. Chem. Soc. Dalton Trans.*, (1979) 547.
[172] R. van Asselt, E.E.C.G. Gielens, R.E. Rülke, K. Vrieze and C.J. Elsevier, *J. Am. Chem. Soc.*, **116** (1994) 977.
[173] N. Koga, *Kagaku to Kogyo*, **40** (1987) 116.
[174] N. Koga and K. Morokuma, *J. Am. Chem. Soc.*, **108** (1986) 6136.
[175] J. Tsuji, *Synthesis*, (1984) 369.
[176] J. Tsuji, *Tetrahedron*, **42** (1986) 4361.
[177] J. Tsuji, *Pure Appl. Chem.*, **58** (1986) 869.
[178] J. Tsuji and I. Minami, *Acc. Chem. Res.*, **20** (1987) 140.
[179] J. Tsuji and T. Mandai, *J. Organomet. Chem.*, **451** (1993) 15.
[180] J. Tsuji, *J. Organomet. Chem.*, **300** (1986) 281.
[181] J. Tsuji, J. Nogami and T. Mandai, *Yuki Gosei Kagaku Kyokaishi*, **47** (1989) 649.
[182] I. Shimizu, M. Oshima, K. Nagasawa, J. Tsuji and T. Mandai, *Yuki Gosei Kagaku Kyokaishi*, **49** (1991) 526.
[183] T. Mandai and J. Tsuji, *Yuki Gosei Kagaku Kyokaishi*, **50** (1992) 908.
[184] T. Hosokawa and S. Murahashi, *Acc. Chem. Res.*, **23** (1990) 49.
[185] T. Hosokawa and S. Murahashi, *Yuki Gosei Kagaku Kyokaishi*, **47** (1989) 636.
[186] G.D. Daves, Jr. and A. Hallberg, *Chem. Rev.*, **89** (1989) 1433.
[187] I.I. Moiseev, *Pure. Appl. Chem.*, **61** (1989) 1755.
[188] W. Oppolzer, *Pure Appl. Chem.*, **62** (1990) 1941.
[189] B. Cazes, *Pure Appl. Chem.*, **62** (1990) 1867.
[190] G.D. Daves, Jr., *Acc. Chem. Res.*, **23** (1990) 201.
[191] T. Hayashi, A. Kubo and F. Ozawa, *Pure Appl. Chem.*, **64** (1992) 421.
[192] J.-E. Bäckvall, *Pure Appl. Chem.*, **64** (1992) 429.
[193] T. Hayashi and Y. Uozumi, *Pure Appl. Chem.*, **64** (1992) 1911.
[194] T.N. Mitchell, *Synthesis*, (1992) 803.
[195] M. Pfeffer, *Pure Appl. Chem.*, **64** (1992) 335.
[196] V.N. Kalinin, *Synthesis*, (1992) 413.
[197] R.J. Perry, *Chemtech*, February (1994) 18.
[198] M. Suzuki, *Yuki Gosei Kagaku Kyokaishi*, **51** (1993) 141.
[199] Y. Masuyama, *Yuki Gosei Kagaku Kyokaishi*, **50** (1992) 202.
[200] Y. Yokoyama and Y. Murakami, *Yuki Gosei Kagaku Kyokaishi*, **52** (1994) 819.
[201] K. Sonogashira and S. Takahashi, *Yuki Gosei Kagaku Kyokaishi*, **51** (1993) 1053.
[202] M. Shibasaki, Y. Sato and K. Kagechika, *Yuki Gosei Kagaku Kyokaishi*, **50** (1992) 826.

[203] L.E. Overman, M.M. Abelman, D.J. Kucera, V.D. Tran and D.J. Ricca, *Pure Appl. Chem.*, **64** (1992) 1813.

[203a] K. Takagi, K. Nakata, Y. Taniguchi and Y. Fujiwara, *Yuki Gosei Kagaku Kyokaishi*, **52** (1994) 809.

[204] J. Tsuji, *Yuki Gosei okaeta Sen-i Kinzoku*, Kagaku Dojin, Kyoto, 1991.

[205] J. Tsuji, *Organic Synthesis with Palladium Compounds*, Springer-Verlag, Berlin, 1980.

[206] B.M. Trost, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel eds., Pergamon Press, Oxford, vol.8, p. 799, 1982.

[207] *Jikken Kagaku Kouza 25, 4th ed., Yuki Gosei VII, Yuki Kinzoku Shiyaku niyoru Gousei*, Japan Chem. Soc. ed., Maruzen, Tokyo, p. 367, 1991.

[208] P.M. Henry, *Adv. Organomet. Chem.*, **13** (1975) 363.

[209] J. Tsuji, *Adv. Organomet. Chem.*, **17** (1979) 141.

[210] A. Heumann, K.-J. Jens and M. Réglier, *Prog. Inorg. Chem.*, **42** (1994) 483.

[211] P.M. Henry, *J. Am. Chem. Soc.*, **86** (1964) 3246.

[212] A.D. Ryabov, *Synthesis*, (1985) 233.

[213] N. Beydoun, M. Pfeffer, *Synthesis*, (1990) 729.

[214] J.E. Hallgren and R.O. Matthews, *J. Organomet. Chem.*, **175** (1979) 135.

[215] J.E. Hallgren, G.M. Lucas and R.O. Matthews, *J. Organomet. Chem.*, **204** (1981) 135.

[216] W.A. Herrmann, C. Brossmer, T. Priermeier and K. Öfele, *J. Organomet. Chem.*, **481** (1994) 97.

[217] F. Kawataka, Y. Kayaki, I. Shimizu and A. Yamamoto, *Organometallics*, **13** (1994) 3517.

[218] R.F. Heck, *Organic Reactions*, **27** (1982) 345.

[219] R.F. Heck, *Acc. Chem. Res.*, **12** (1979) 146.

[219a] M. Kudo, *Shokubai*, **36** (1994) 580.

[219b] W. Cabri and I. Candiani, *Acc. Chem. Res.*, **28** (1995) 2.

[219c] A. de Meijere and F.E. Meyer, *Angew. Chem. Int. Ed. Engl.*, **33** (1994) 2379.

[219d] N.A. Bumagin, V.V. Bykov, L.I. Sukhomlinova, T.P. Tolstaya and I.P. Beletskaya, *J. Organomet. Chem.*, **486** (1995) 259.

[220] M. Suzuki, J.-C. Lim and T. Saegusa, *Organometallics*, **23** (1990) 1574.

[220a] Y. Kubota, K. Takeuchi, T. Hanaoka and Y. Sugi, *Bull. Chem. Soc. Japan*, **67** (1994) 563.

[221] H. Kataoka, T. Yamada, K. Goto and J. Tsuji, *Tetrahedron*, **43** (1987) 4107.

[222] A. Yoshioka and T. Yamada, *Yuki Gosei Kagaku Kyokaishi*, **48** (1990) 56.

[223] W.E. Billups, W.E. Walker and T.C. Shields, *J. Chem. Soc. Chem. Commun.*, (1971) 1067.

[224] B.M. Trost and Y. Shi, *J. Am. Chem. Soc.*, **115** (1993) 9421.

[225] B.M. Trost, G.J. Tanoury, M. Lautens, C. Chan and D.T. MacPherson, *J. Am. Chem. Soc.*, **116** (1994) 4255.

[226] B.M. Trost, D.L. Romero and F. Rise, *J. Am. Chem. Soc.*, **116** (1994) 4268.

[227] M. Iwasaki, Y. Ishi and M. Hidai, *Yuki Gosei Kagaku Kyokaishi*, **49** (1991) 909.

[228] E. Drent, P. Arnoldy and P.H.M. Budzelaar, *J. Organomet. Chem.*, **455** (1993) 247.

[229] E. Drent, P. Arnoldy and P.H.M. Budzelaar, *J. Organomet. Chem.*, **475** (1994) 57.

21 Organoplatinum Compounds

21.1 INTRODUCTION

Speaking of platinum, there is cisplatin (*cis*-$Pt(NH_3)_2Cl_2]$) [1]. The cisplatin is a compound having a strong medicinal action on cancers or tumors of bladder, lung, head, neck, cervix, testicles, ovary, etc. However, it has some side effects of nephrotoxicity, emesis, nausea, etc. Therefore, many derivatives have been synthesized and some of these compounds are organoplatinum compounds having a Pt–C bo#nd. The side effects of these compounds are less than those of cisplatin, but there is no better a compound than cisplatin regarding its anticancer properties.

As platinum is in the same group as nickel and palladium, platinum compounds show similar reactivity as nickel and palladium compounds. However, platinum compounds do not have strong characteristic properties. Thus, platinum compounds are not widely used like palladium and nickel compounds in organosynthetic reactions. Platinum has a strong affinity to hydrogen and oxygen, and platinum black and platinum compounds are used as catalysts for reduction and oxidation. In particular, they are used for hydrogen catalysts.

21.2 PLATINUM

Platinum belongs to group 10 of the periodic table, the same as nickel and palladium. The outer electron configuration is $5d^9s^1$. It exists as 0.001 ppm in the Earth's crust, which is in similar amounts to gold (0.0011 ppm), silver (0.07 ppm) and palladium (0.006 ppm) of the precious elements [2,3]. Platinum is produced from anode slim in the electrolytic refining of crude copper and crude nickel as described in the organoruthenium chapter (16), the organorhodium chapter (18) and the organopalladium chapter (20). The anode slim is reacted with aqua regia, and then gold, platinum and palladium are dissolved. The nitric acid is removed by repeating the following process; hydrochloric acidic is added to the solution and evaporated to dryness. Then iron(III) sulfate is added to precipitate gold. Ammonium chloride is added to the filtrate to precipitate $(NH_4)_2PtCl_6$. The precipitate is separated and heated at 700 °C to produce a sponge platinum. The high purity platinum is produced by repeating the previous process or by the electrolysis of the H_2PtCl_6 solution [4–7].

Platinum remains bright in air at all temperatures, but finely divided platinum can be oxidized to platinum oxide at about 500 °C in oxygen, preferably under pressure. Sulfur dioxide does not attack platinum at elevated temperatures. As a finely divided catalyst, platinum functions for years at 600 °C in hot SO_2–SO_3 mixtures in the manufacturing of sulfuric acid. Hydrogen sulfide has only a slight effect upon hot platinum, i.e., a slight weight gain is observed after 12 h exposure at 1000 °C. Fused alkalis are somewhat corrosive to platinum, particularly in the presence of oxygen or oxidizing agents; barium and potassium hydroxides are the most corrosive. At room temperature, platinum is resistant to practically all reagents except aqua regia. Platinum is attacked by chlorine at above 250 °C, but the attack by hydrogen chloride is negligible at temperatures lower than 1000 °C. Bromine and iodine do not attack in the 600–800 °C range; however, above 1200 °C the attacking rates by chlorine, bromine, and iodine are about equal [4]. Platinum does not react with carbon monoxide directly, which is different from nickel. Platinum absorbs over 100 times its volume of hydrogen and also absorbs large quantities of oxygen. Thus, platinum is used as an oxidation or reduction catalyst. The properties of platinum are shown in Table 20.1 [3,4].

As platinum is stable to most reagents, it is used in crucibles for analytical chemistry. But, B, Si, Pb, P, As, Sb and Bi, produce low melting point compounds with platinum under a reductive atmosphere, so platinum vessels are not used with these elements. A main use of platinum is ornaments, thermocouples, crucibles, electric contact points, electrodes, electric furnaces, chemical apparatuses, dental materials, catalysts for hydrogenation, dehydrogenation, isomerization, etc. Platinum black is used as a catalyst in the petroleum-refining industries and for catalytic car waste gas treatment [3–10].

Table 21.1 Properties of platinum [3,4]

Property	Value
melting point, °C	1769
boiling point, °C	4170
crystal structure	face-centered cubic
density, 20 °C, g/cm^3	21.45
specific heat at 0 °C, J g^{-1}	0.1314
linear coefficient of thermal expansion at 20 °C, K^{-1}	9.1×10^{-6}
electrical resistivity at 20 °C, $\mu\Omega$·cm	10.6
hardness	
Mohs scale	4.3
Vickers hardness, annealed	38–40
thermal conductivity, Wm^{-1}K^{-1}	71.1
mass susceptibility, cm^{3}g^{-1}	9.0×10^{-6}

21.3 PREPARATION OF ORGANOPLATINUM COMPOUNDS

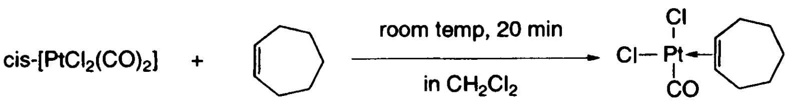
As organoplatinum compounds have similar properties to organopalladium compounds [2], they are prepared by similar methods to those of organopalladium compounds. Organoplatinum compounds are prepared mainly by the following seven reactions.

(1) Reactions with unsaturated hydrocarbons
(2) Reactions with organometallic compounds
(3) Reactions with unsaturated organoplatinum compounds
(4) Carbonylations
(5) Oxidative addition by organic halides
(6) Cyclometalations
(7) Others

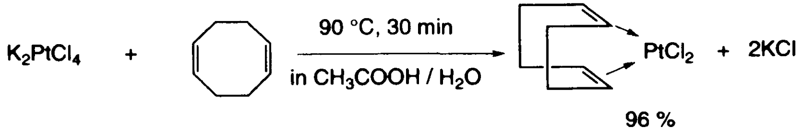
21.3.1 REACTIONS WITH UNSATURATED HYDROCARBONS

Organoplatinum compounds easily react with unsaturated hydrocarbons such as monoolefins, diolefins and acetylenes to afford the π-complexes. For example, reactions are shown in eqs. (21.1)–(21.5). The compound shown in eq. (21.1) is the Zeise salt of an ethylene–platinum complex found at first as an organotransition metal compound [11–17].

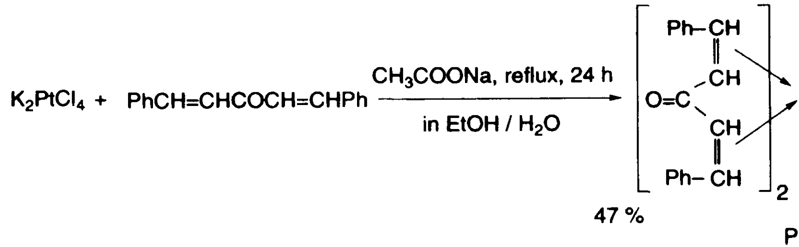
$$K_2PtCl_4 + CH_2{=}CH_2 + H_2O \xrightarrow{SnCl_2,\ 40-45\ ^\circ C} \underset{\textbf{Zeise salt}\ \ \textbf{86 \%}}{K[(CH_2{=}CH_2)PtCl_3)]{\bullet}H_2O} + HCl \qquad (21.1)$$

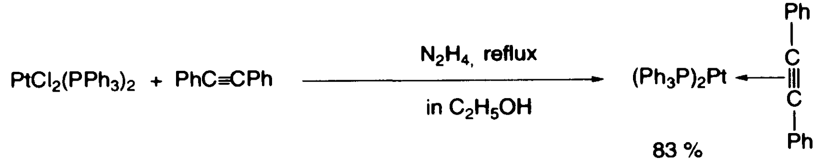


(21.2)



(21.3)


(21.4)


(21.5)

$$PtCl_2(PPh_3)_2 + PhC\equiv CPh \xrightarrow[\text{in } C_2H_5OH]{N_2H_4,\ \text{reflux}} (Ph_3P)_2Pt \leftarrow PhC\equiv CPh \quad 83\ \%$$

As shown in eqs. (21.3) and (21.4), the reactions of platinum halides with diolefins afford diolefin platinum complexes. In these diolefin platinum complexes, the order of the stability of the four compounds is shown in Figure 21.1 [18]. The figure shows that the complexes of cyclic diolefins, such as cycloocta-1,5-diene and dicyclopentadiene, are more stable than those of linear unsaturated compounds.

21.3.2 REACTIONS WITH ORGANOMETALLIC COMPOUNDS

Organometallic compounds such as organolithium compounds, Grignard reagents, organotin compounds and organothallium compounds react with platinum halides to afford organoplatinum compounds [11,13,19–27]. For example, reactions are shown in eqs. (21.6)–(21.13). The order of the stability of the many compounds obtained by these reaction methods are as follows:

C≡CH < alkyl < phenyl ~*p*-substituted phenyl < C≡CPh < *o*-substituted phenyl

In these compounds, the *o*-substituted phenyl is the most stable, the cause of which is thought to be that the substituent at the *ortho*-position protects against attack on the platinum [24].

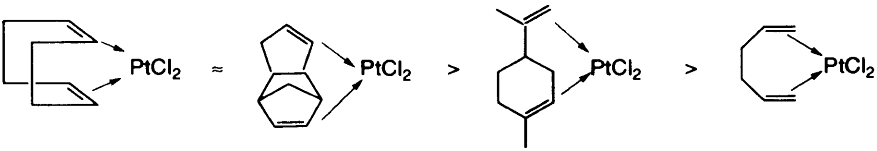
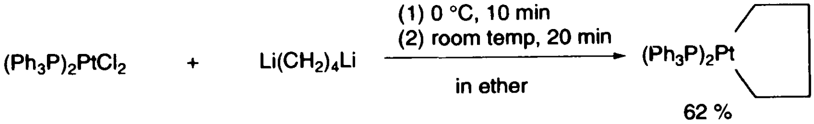


Figure 21.1 The order of stabilities of dieneplatinum complexes [18].



(21.6)

$$trans\text{-}[PtCl_2(PEt_3)_2] + MeMgI \xrightarrow[\text{in ether / benzene}]{\text{20 °C, 1 h}} \underset{90\ \%}{trans\text{-}MePtI(PEt_3)_2} \qquad (21.7)$$

$$cis\text{-}[PtCl_2(PPh_3)_2] + 2n\text{-}BuLi \xrightarrow[\text{in ether / hexane}]{\text{room temp, 30 min}} \underset{90\ \%}{cis\text{-}[n\text{-}Bu_2Pt(PPh_3)_2]} \qquad (21.8)$$

$$K_2PtCl_6 + 3MeMgI \xrightarrow[\text{in ether / benzene}]{\text{0 °C to room temp}} \underset{80\ \%}{Me_3PtI} \qquad (21.9)$$

$$PtCl_2 + C_3H_7MgCl + C_5H_5Na \xrightarrow[\text{in ether / THF}]{\text{20 °C, 1 h}} \underset{29\ \%}{\eta^5\text{-}C_5H_5Pt(\eta^3\text{-}C_3H_5)} \qquad (21.10)$$

$$PtCl_2 + 2C_3H_5MgBr \xrightarrow[\text{in ether}]{\text{−78 °C, 20 h}} (\eta^3\text{-}C_3H_5)_2Pt \qquad (21.11)$$

$$trans\text{-}[PtCl_2(PEt_3)_2] + Me_3SnC{\equiv}CMe \xrightarrow[\text{in THF}]{\text{reflux, 48 h}} \underset{80\ \%}{trans\text{-}[(MeC{\equiv}C)PtCl(PEt_3)_2]} \qquad (21.12)$$

$$cis\text{-}[PtCl_2(CO)(PMePh_2)] + CpTl \xrightarrow[\text{in ether}]{\text{room temp, 1 h}} \underset{30\ \%}{(\eta^1\text{-}C_5H_5)Pt(CO)(Cl)(PMePh_2)} \qquad (21.13)$$

21.3.3 REACTIONS WITH UNSATURATED HYDROCARBON PLATINUM COMPOUNDS

The platinum compounds of unsaturated hydrocarbons such as 1,5-cyclooctadiene, ethylene and allyl compounds are used as the raw material for substitution reactions. However, the synthetic examples of organoplatinum compounds are less than those of organonickel compounds. For example, reactions are shown in eqs. (21.14)–(21.18) [26–31].

$$(\eta^3\text{-}C_3H_5)_2Pt \quad + \quad 2PPh_3 \xrightarrow[\text{in pentane}]{0\ ^\circ\text{C, 20 h}} (\eta^3\text{-}C_3H_5)_2Pt(PPh_3)_2 \qquad (21.14)$$

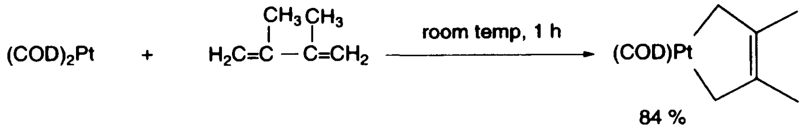
mp 118 - 122 °C

$$(COD)PtCl_2 \quad + \quad C_8H_{12} \xrightarrow[\text{in ether}]{Li_2C_8H_8,\ -50\ ^\circ\text{C} \\ -35\ ^\circ\text{C, 1.5 h}} (COD)_2Pt + LiCl + C_8H_8$$

31 %

$$(COD)_2Pt \quad + \quad 3C_2H_4 \xrightarrow[\text{in light petroleum}]{0\ ^\circ\text{C, stirring}} (C_2H_4)_3Pt \qquad (21.15)$$

60 %



$$(COD)_2Pt + H_2C{=}\overset{CH_3}{C}-\overset{CH_3}{C}{=}CH_2 \xrightarrow{\text{room temp, 1 h}} (COD)Pt$$

(21.16)

$$(C_2H_4)Pt(PPh_3)_2 \quad + \quad PhCOCl \xrightarrow{\text{room temp, 1 h}} (PhCO)PtCl(PPh_3)_2 \qquad (21.17)$$

93 %

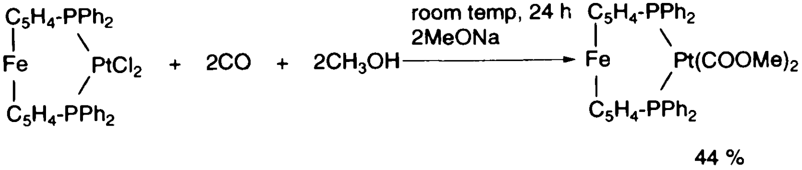
$$(C_2H_4)Pt(PPh_3)_2 \quad + \quad MeI \xrightarrow[\text{in benzene}]{25\ ^\circ\text{C}} MePtI(PPh_3)_2 \qquad (21.18)$$

21.3.4 CARBONYLATIONS

Metals such as Fe, Ni, Ru and Rh react directly with carbon monoxide, but platinum together with palladium [2] is not able to react directly with carbon monoxide. As shown in eqs. (21.19)–(21.20), platinum compounds are able to react with carbon monoxide in the presence of phosphine via phosphine complexes [32]. On the other hand, a phosphine complex reacts with carbon monoxide in the presence of alcohol to afford an ester as shown in eq. (21.21) [33].

$$Na_2PtCl_4 + 2PPh_3 + CO \xrightarrow[\text{in EtOH / THF}]{N_2H_4{\bullet}H_2O\text{, stirring 12 h}} \underset{89\ \%}{Pt(CO)(PPh_3)_3} \qquad (21.19)$$

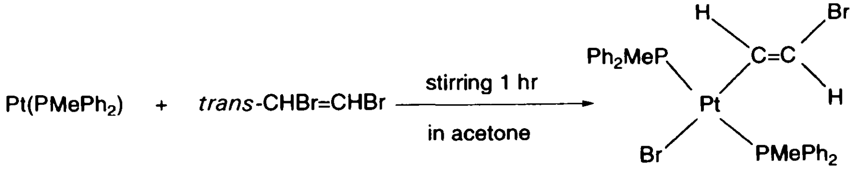
$$Pt(PPh)_4 + 2CO \xrightarrow[\text{in acetone}]{\text{stirring 1 h}} \underset{49\ \%}{Pt(CO)_2(PPh_3)_2} \qquad (21.20)$$



$$Fe(C_5H_4\text{-}PPh_2)_2PtCl_2 + 2CO + 2CH_3OH \xrightarrow{\text{room temp, 24 h}\ \ 2MeONa} \underset{44\ \%}{Fe(C_5H_4\text{-}PPh_2)_2Pt(COOMe)_2} \qquad (21.21)$$

21.3.5 OXIDATIVE ADDITION REACTIONS WITH ORGANIC HALIDES

The oxidative addition reactions of organic halides to platinum phosphine compounds easily proceed. For example, reactions are shown in eqs. (21.22) and (21.23) [26,34]. The vinyl bromide derivative obtained by the reaction shown in eq. (21.22) is liable and it gives $PtBr_2(PMePh_2)_2$ and acetylene by elimination [34].

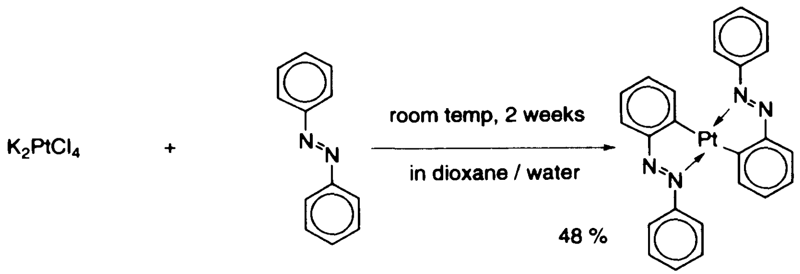


(21.22)

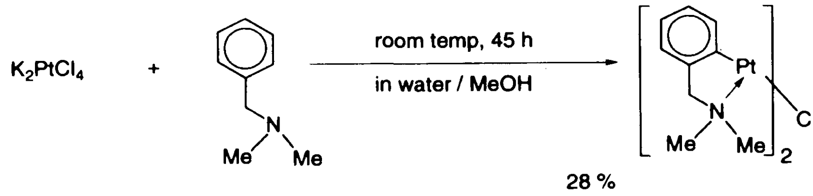
$$cis\text{-}Me_2Pt(PMe_2Ph)_2 + MeCl \xrightarrow[\text{in sealed tube}]{20\ ^\circ C\text{, 7 weeks}} Me_3PtCl(PMe_2Ph) \qquad (21.23)$$

21.3.6 CYCLOMETALATIONS

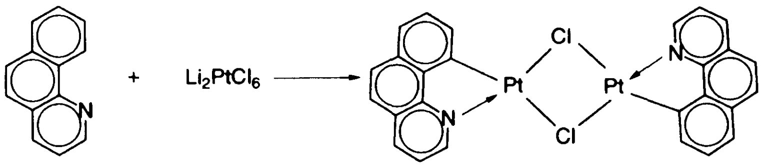
Cyclometalations on the various kinds of metal compounds easily proceed to give stable compounds [36]. These reactions affords selectively five-membered ring compounds, which are very stable [35]. Cyclometalations on platinum compounds easily proceed to give stable organoplatinum compounds [36–89]. For example, reactions are shown in eqs. (21.24)–(21.27) [36,37,41,43].



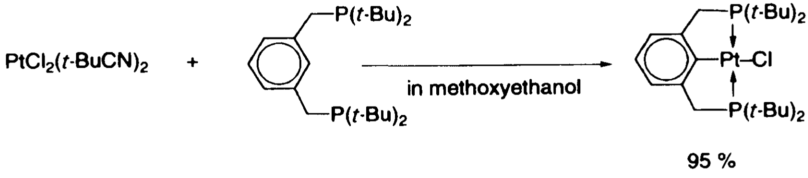
(21.24)



(21.25)



(21.26)



(21.27)

21.3.7 OTHERS

Isonitriles, acetylenes having an active hydrogen or alcohols react easily with platinum compounds to afford the organoplatinum compounds. For example, reactions are shown in eqs. (21.28)–(21.31) [11,90–94]. The reaction with ethyl alcohol shown in eq. (21.30), yields the Zeise salt by dehydration. This is the reaction that Zeise published in 1830 [93].

$$\textit{trans}\text{-}[Pt_2Cl_4(PEt_3)_2] + 2PhNC \xrightarrow[\text{in benzene}]{25^\circ\text{ C, 1 h}} 2\textit{cis}\text{-}[(PhNC)PtCl_2(PEt_3)] \quad (21.28)$$

85 %

$$\textit{trans}\text{-}[PtCl_2(PEt_3)_2] + 2HC{\equiv}CH \xrightarrow{CuI\ /\ HNEt_2} \underset{90\ \%}{\textit{trans}\text{-}[(HC{\equiv}C)_2Pt(PEt_3)_2]} \quad (21.29)$$

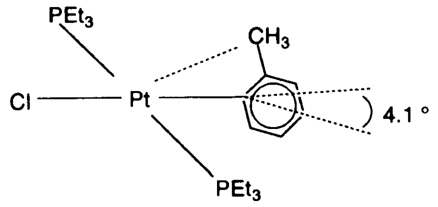
$$K_2PtCl_6 + CH_3CH_2OH \longrightarrow \underset{\text{Zeise salt}}{K[(CH_2{=}CH_2)PtCl_3]} \quad (21.30)$$

$$Na_2PtCl_6 + PhCH_2CH_2OH \longrightarrow Na[(PhCH{=}CH_2)PtCl_3] \quad (21.31)$$

21.4 STRUCTURES OF ORGANOPLATINUM COMPOUNDS

Platinum belongs to group 10 of the periodic table, the same as nickel and palladium. These organometallic compounds are liable to form a square planar structure with four-coordination. For example, organoplatinum compounds ((o-$CH_3C_6H_4$)$PtCl(PEt_3)_2$ [95]) shown in Figure 21.2 shows the square-planar structure with four-coordination. The benzene ring is nearly perpendicular to the Pt coordination plane, and the benzene ring is tilted away from the Pt coordination plane by 4.1° by the bulky methyl group. The Pt–CH_3 distance is maintained at approximately the sum of the van der Waals radii [95].

Articles on the structures apart from square planar in organoplatinum compounds are few. Square pyramidal structure with five-coordination [82–84], trigonal planar structure with three-coordination [96,97], and octahedral structure with six-coordination [96] are all alternatives to the square planar structure. For example, the square pyramidal structure, trigonal planar structure and octahedral



square planar

Pt-Cl = 2.412 Å
Pt-P^1 = 2.313 Å
Pt-P^2 = 2.269 Å
Pt-C = 2.052 Å
Pt-CH$_3$ = 3.32 Å

Figure 21.2 Molecular structure of (o-CH_3-C_6H_4)$PtCl(PEt_3)_2$ [95].

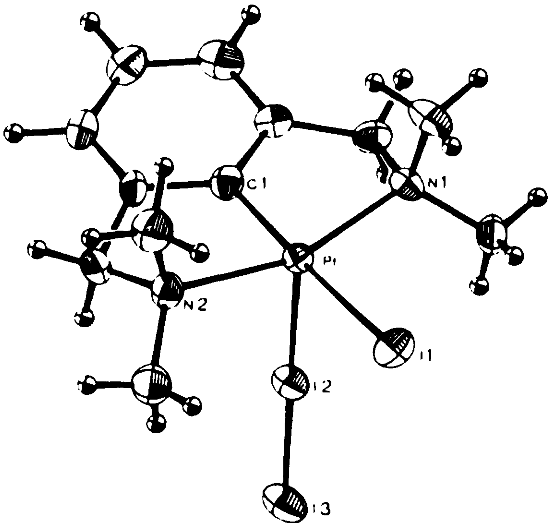


Figure 21.3 Molecular structure of $C_6H_3(CH_2NMe_2)_2PtI(I_2)$ [82].

structure are shown in Figure 21.3 [82], Figure 21.4 [96] and Figure 21.5 [98], respectively

The sandwich structure of a benzene ring and cyclobutadiene ring is shown in Figure 21.6 [99]. The outer electrons by coordination of these two rings become 20-electrons. Therefore the platinum atom becomes Pt^{2+} [99].

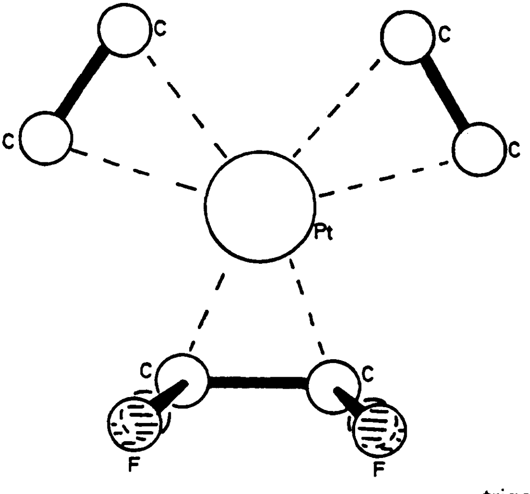


Figure 21.4 Molecular structure of $(C_2H_4)_2(C_2F_4)Pt$ [96].

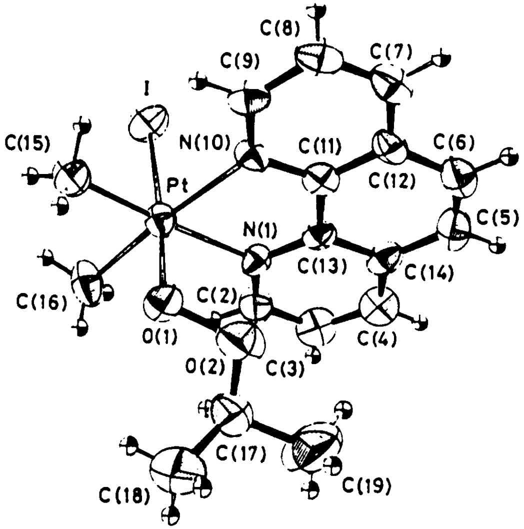


Figure 21.5 Molecular structure of dimethyl(1,10-phenanthroline)platinum(II) [98].

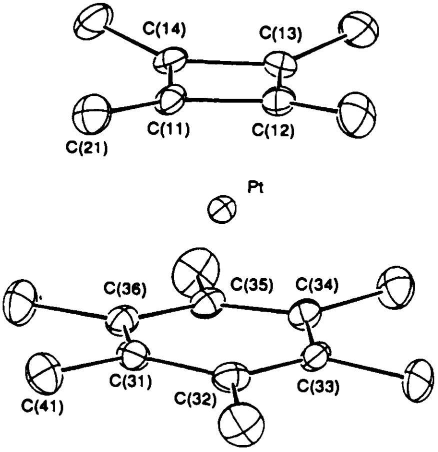


Figure 21.6 Molecular structure of $[\eta^6\text{-}(C_6Me_6)(\eta^4\text{-}C_4Me_4)Pt]^{2+}[CF_3SO_3]^-{}_2\cdot Me_2CO$ [99].

21.5 REACTIONS OF ORGANOPLATINUM COMPOUNDS

As the reactions of organoplatinum compounds, the following five reactions are noted.

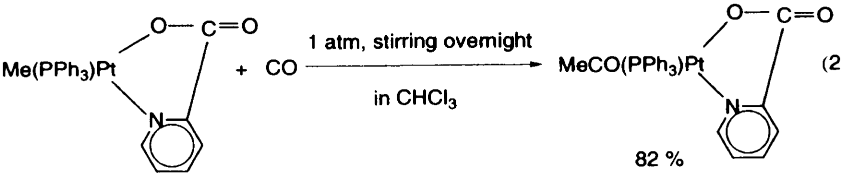
(1) Insertions
(2) Oxidative additions

(3) Coupling reactions of olefin complexes
(4) Addition reactions of nucleophilic reagents
(5) Formation reactions of platinum carbene complexes

21.5.1 INSERTIONS

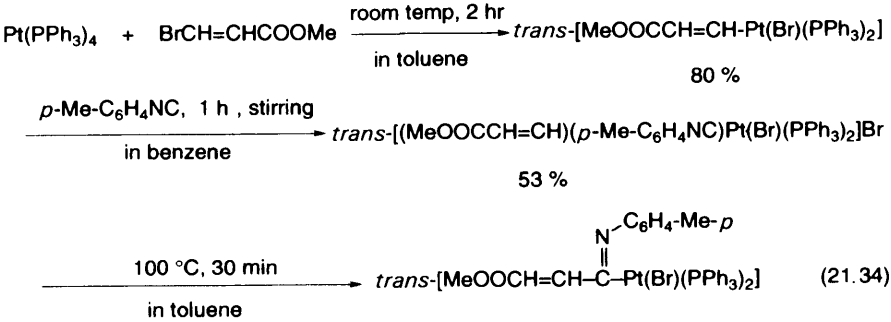
In organoplatinum compounds, insertion into the metal–carbon bond proceeds similar to the organopalladium compounds [100–106]. For example, if methyl platinum compounds react with carbon monoxide, the carbon monoxide inserts into the Pt–C bond to afford the methylcarbonylplatinum complexes as shown in eqs. (21.32) and (21.33) [100,101].

$$\textit{trans}\text{-MePtCl}(\text{PEt}_3)_2 + \text{CO} \xrightarrow[\text{in light petroleum}]{\text{1 atm, 15 °C, 24 h}} \textit{trans}\text{-}(\text{MeCO})_2\text{PtCl}(\text{PEt}_3)_2 \qquad (21.32)$$



(21.33)

Isocyanate and sulfur dioxide also insert into the Pt–C bond as shown in eqs. (21.34) and (21.35), respectively [102,103].



$$\text{Pt}(\text{PPh}_3)_4 + \text{BrCH=CHCOOMe} \xrightarrow[\text{in toluene}]{\text{room temp, 2 hr}} \underset{80\ \%}{\textit{trans}\text{-}[\text{MeOOCCH=CH-Pt(Br)}(\text{PPh}_3)_2]}$$

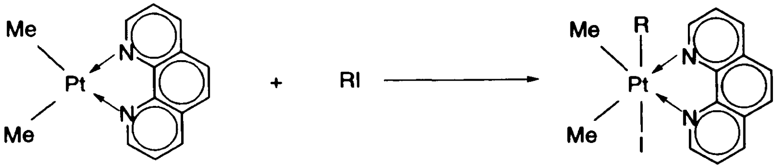
$$\xrightarrow[\text{in benzene}]{p\text{-Me-C}_6\text{H}_4\text{NC, 1 h, stirring}} \underset{53\ \%}{\textit{trans}\text{-}[(\text{MeOOCCH=CH})(p\text{-Me-C}_6\text{H}_4\text{NC})\text{Pt(Br)}(\text{PPh}_3)_2]\text{Br}}$$

$$\xrightarrow[\text{in toluene}]{\text{100 °C, 30 min}} \textit{trans}\text{-}[\text{MeOOCH=CH-}\overset{\overset{\text{N}\diagup\text{C}_6\text{H}_4\text{-Me-}p}{\|}}{\text{C}}\text{-Pt(Br)}(\text{PPh}_3)_2] \qquad (21.34)$$

$$\textit{trans}\text{-PhPtCl}(\text{PEt}_3)_2 + \text{SO}_2 \xrightarrow[\text{in a Crius tube}]{\text{45 °C, ovemight}} \textit{trans}\text{-}[\text{PhSO}_2\text{PtCl}(\text{PEt}_3)_2] \qquad (21.35)$$

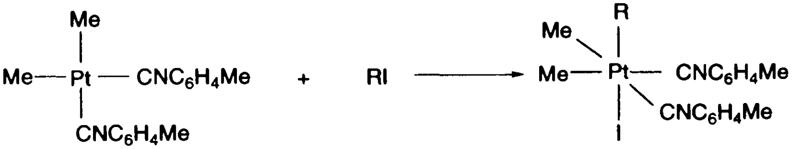
21.5.2 OXIDATIVE ADDITIONS

Organoplatinum compounds are prepared by the oxidative addition of organic halides described above. Platinum compounds become active by coordinating with compounds having lone pair electrons such as amines and phosphines, or by bonding with isocyanate compounds. Then their oxidative additions [98,107–110] proceed as shown in eqs. (21.36) [96] and (21.37) [107]. In the former reaction, if



(21.36)

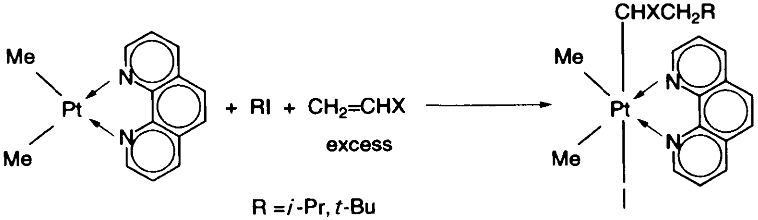
R = Me, Et, *n*-Pr, *i*-Pr



(21.37)

RI = MI, CF_3I

oxygen presents in the reaction system, the reaction yields the peroxides (e.g., R = *i*-PrOO, Me_2(*i*-PrOO)PtI(1,10-phenanthroline) by the autoxidation of the alkyl group [98]. Further, in the presence of alkenyl halides, the reaction yields the alkenyl halide inserted products as shown in eq. (21.38). The reaction is thought to proceed by a free radical mechanism [109].

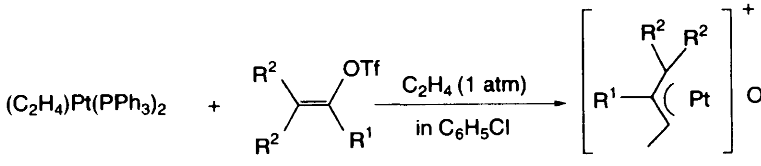


(21.38)

R = *i*-Pr, *t*-Bu
X = CN, CHO, C(=O)Me, CHO

21.5.3 COUPLING REACTIONS OF OLEFIN PLATINUM COMPLEXES

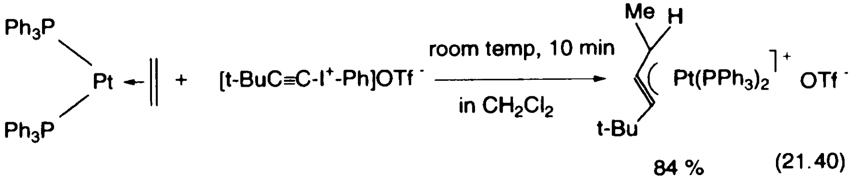
If olefin platinum complexes react with olefins or acetylenes, the coupling reactions proceed [111–113]. In the reaction shown in eq. (21.39), the reaction mechanism is thought to be that first the σ-vinyl compound of olefin is produced, followed by ethylene inserts to the σ-vinyl bond to afford the π-allyl complex. The reaction with acetylene affords the η^3-propagyl/allenyl complex as shown in eq. (21.40) [113].



(21.39)

R^1, R^2 = H, Me, *t*-Bu

TfOH = CF_3SO_2OH, trifluoromethanesulfonic acid

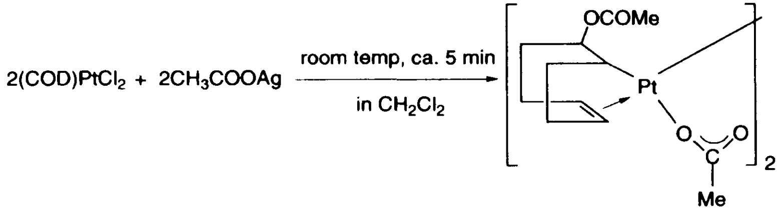


(21.40)

allenyl complex

21.5.4 ADDITION REACTIONS WITH NUCLEOPHILIC REAGENTS

Diene platinum complexes such as (COD)$PtCl_2$, (NBD)$PtCl_2$ (NBD = norbornadiene) and (DPD)$PtCl_2$ (DPD = dicyclopentadiene) easily react with nucleophilic reagents such as carboxylates, alkoxylates, amines and hydroxides to afford the addition products in high yields [8,114–117]. For example, reactions are shown in eqs. (21.41)–(21.43).

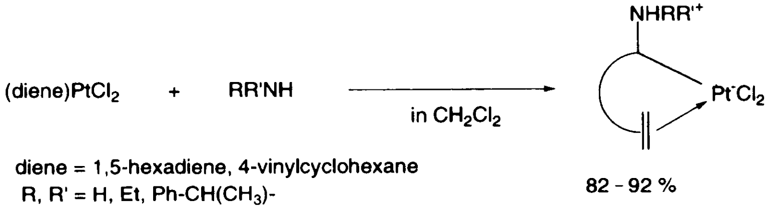


(21.41)

(21.42)

R = Me, Et

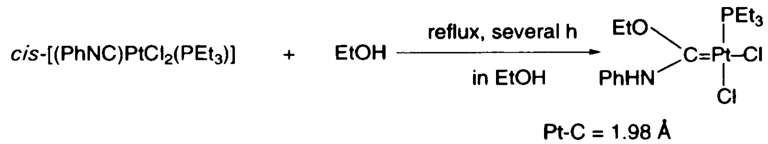
diene = cycloocta-1,5-diene (COD), tetraphenylcyclobutadine, bicyclo[2,2,1]heptadiene (norbornadiene,NBD), dicyclopentadiene (DPD)



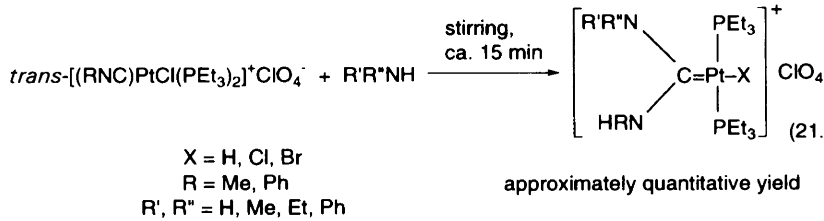
(21.43)

21.5.5 FORMATION REACTIONS OF PLATINUM CARBENE COMPLEXES

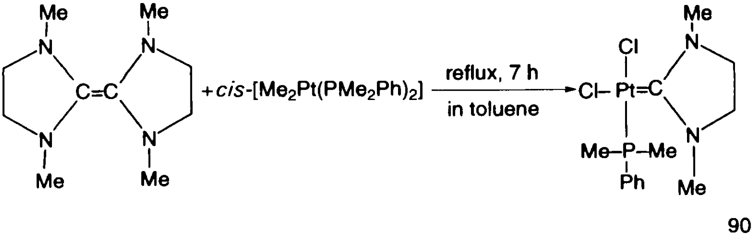
Platinum compounds yield various kinds of carbene complexes [118–137]. For example, if isocyanate platinum compounds react with alcohols or amines, the carbon of the isocyanate bonds to the hetero atom to afford the reactive CXY (X and Y are hetero atoms) group, and the carbene complex yields as shown in eqs. (21.44) [119,127] and (21.45) [120]. On the other hand, as shown in eq. (21.46) [121], the platinum carbene complexes are also obtained by the reaction of cyclic XYC = CXY with platinum compounds on heating for a long time. In these carbene complexes, the *cis*-isomer is more stable than the *trans*-isomer as shown in eq. (21.47), the *trans*-isomers being isomerized to the *cis*-isomer at around 200 °C [125]. The Pt—C bond length of these carbene complexes is about 2.00 Å: slightly shorter than 2.16 Å, the sum of the covalent radii of the Pt—C bond (Pt = 1.39 Å, C = 0.77 Å).



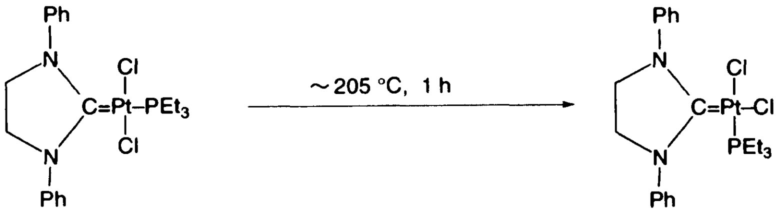
(21.44)



(21.45)



(21.46)



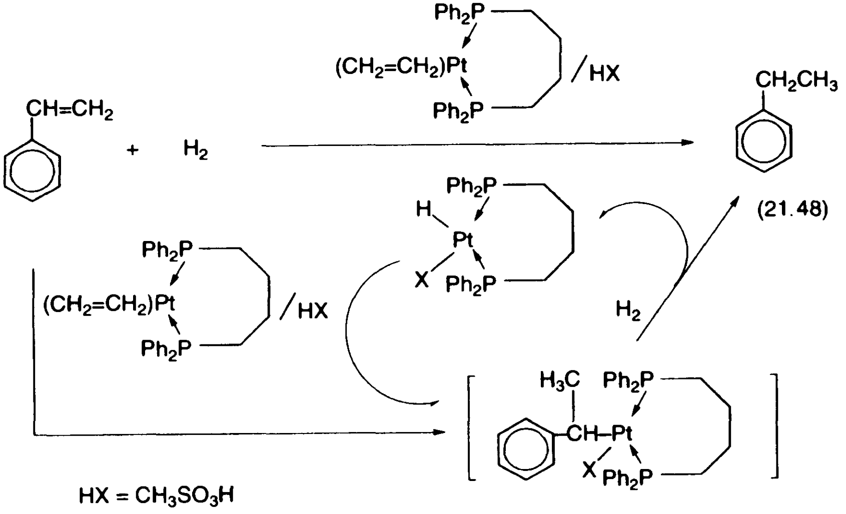
(21.47)

21.6 ORGANOSYNTHETIC REACTIONS WITH PLATINUM COMPOUNDS

The applications of organosynthetic reactions with platinum compounds are much less than those with palladium compounds. However, platinum has a high occlusion property to hydrogen and adhesion property to oxygen. Then the platinum atom has a strong affinity to hydrogen and oxygen, and a π-coordinating property to olefins. Hence, reduction and oxidation reactions are liable to proceed with platinum catalysts as described above.

Recently, Whitesides and co-workers [134–140] have studied the hydrogenation reduction of diolefin alkylplatinum complex ((diene)PtR_2) with platinum black as shown in Figure 21.7. (Diene)PtR_2 attached at first on the surface of platinum, then alkane and cycloalkane is yielded by bonding with hydrogen which is bonded on the surface of platinum [134]. The alkyl group is reduced much more easily than COD on the reduction of (COD)PtR_2 [136].

In the hydrogenation reaction of styrene, reaction mechanisms are thought to be as shown in eq. (21.48) i.e., at first the unsaturated bond of styrene forms a σ-coordination after forming a π-coordination to the platinum, then hydrogen acts to



(21.48)

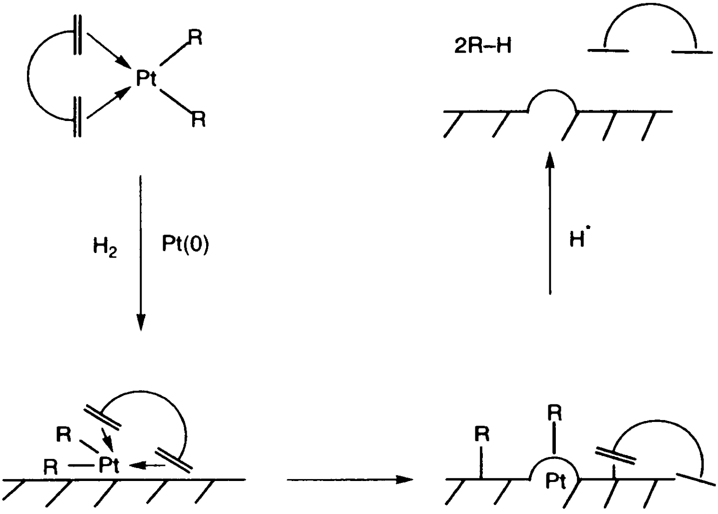
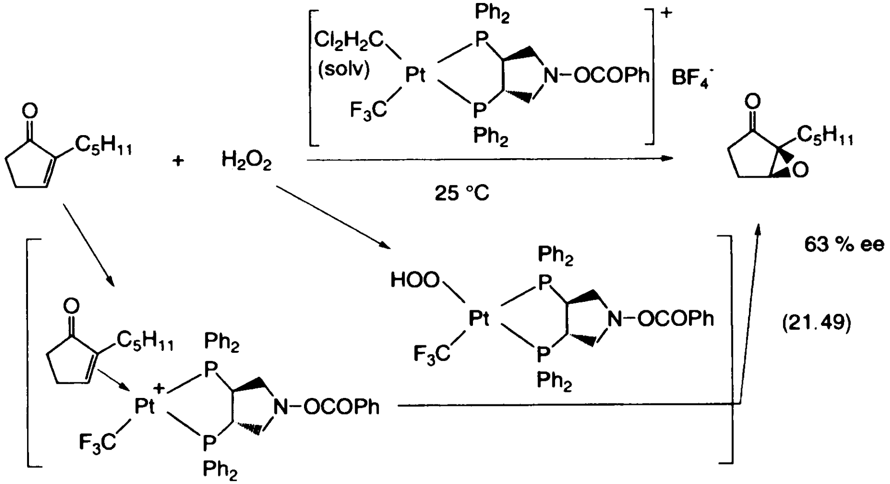


Figure 21.7 Mechanism proposed for the heterogenous hydrogenation of (diolefin)dialkylplatinum(II) complexes [134].

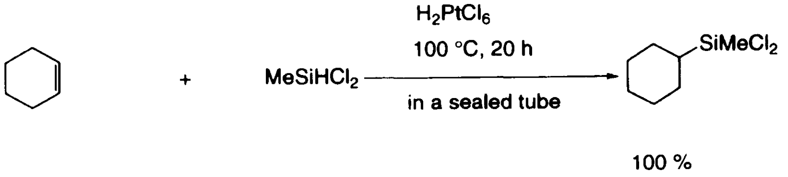
the σ-coordination compounds to afford ethylbenzene and a platinum hydrogen complex [141].

Oxidation of an unsaturated compound with hydrogen peroxide has been reported as examples of oxidation reactions [142,143]. For example, the oxidation of a cyclopentenone derivative with a chiral organoplatinum compound affords the epoxide in 63% ee yield as shown in eq. (21.49) [143].



(21.49)

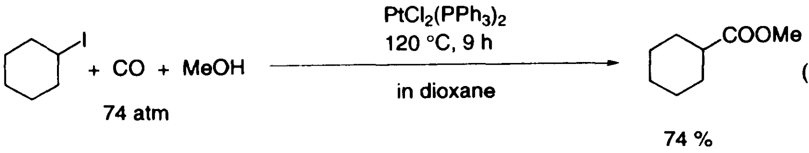
Finally, hydrosilylation, carboxylation and carboxyesterification reactions are shown as a catalytic reaction with platinum compounds as shown in eqs. (21.50)–(21.52) [144–147].



(21.50)

$$CH_3(CH_2)_9CH{=}CH_2 + CO + H_2O \xrightarrow[\text{in acetone}]{H_2PtCl_6,\ SiCl_2,\ 90\ ^\circ C,\ 3000\ psi,\ 1\text{-}2\ h} CH_3(CH_2)_{10}CH_2COOH \qquad (21.51)$$

conversion 100 %
yield 74 %
linear selectivity 86 %



(21.52)

REFERENCES

- [1] *Platinum Metal Rev.*, **31** (1987) 193.
- [2] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
- [3] *Kagaku Daijiten*, Tokyo Kagaku Doojin, Tokyo, p. 1781, 1989.
- [4] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., John Wiley, New York, vol. 18, p. 228, 1980.
- [5] *Rikagaku Jiten*, Iwanami Shoten, Tokyo, 4th ed., p. 983, 1987.
- [6] *Sekai Dai Hyakkajiten*, Heibonsha, Tokyo, vol. 22, p. 596, 1988.
- [7] *Sekai Kagaku Daijiten, Technopia (Encyclopedia of Science and Technology)*, Koudansha, Tokyo, vol. 14, p. 302, 1977.
- [8] *The Merck Index*, 11th ed., 1989.
- [9] H.K. Straschril and J.G. Cohn, *Platinum Group Metals, Compounds* in ECT 2nd ed., vol. 15, p. 861.
- [10] F.A. Coton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., John Wiley, New York, 1988.
- [11] F.R. Hartley, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 6, p. 471, 1982.

[11a] *Jikken Kagaku Kouza 18, 4th ed., Yuki Kinzoku Sakutai*, Japan Chem. Soc. ed., Maruzen, Tokyo, p. 412, 1991.

[12] P.B. Chock, J. Halpern and F.E. Paulik, *Inorg. Syntheses*, **14** (1973) 90.

[13] J.X. McDermott, J.F. White and G.M. Whitesides, *J. Am. Chem. Soc.*, **98** (1976) 6521.

[14] D. Drew and J.R. Doyle, *Inorg. Syntheses*, **13** (1972) 47.

[15] W.J. Cherwinski, B.F.G. Johnson and J. Lewis, *J. Chem. Soc. Dalton Trans.*, (1974) 1405.

[16] E.O. Greaves, C.J.L. Lock and P.M. Maitlis, *Can. J. Chem.*, **46** (1968) 3879.

[17] D.B. Dell'Amico, F. Calderazzo, N. Pasqualetti, C. Maichele-Mössmer, J. Strähle and K. Wurst, *Organometallics*, **13** (1994) 1582.

[18] J. Chatt, L.M. Vallarino and L.M. Venanzi, *J. Chem. Soc.*, (1957) 2496.

[19] J. Chatt and B.L. Shaw, *J. Chem. Soc.*, (1957) 705.

[20] G.M. Whitesides, J.F. Gaasch and E.R. Stedronsky, *J. Am. Chem. Soc.*, **94** (1972) 5258.

[21] J.C. Baldwin and W.C. Kaska, *Inorg. Chem.*, **14** (1975) 2020.

[22] B.E. Mann, B.L. Shaw and G. Shaw, *J. Chem. Soc. A*, (1971) 3536.

[23] D.E. Clegg and J.R. Hall, *Inorg. Syntheses*, **10** (1967) 71.

[24] J. Chatt and B.L. Shaw, *J. Chem. Soc.*, (1959) 4020.

[25] J.K. Becconsall, B.E. Job and S. O'Brien, *J. Chem. Soc. A*, (1967) 423.

[26] J.D. Ruddick and B.L. Shaw, *J. Chem. Soc. A*, (1969) 2801.

[27] R.J. Cross, L.J. Farrugia and K.E.A. Kuma, *J. Organomet. Chem.*, **471** (1994) 273.

[28] C. Detellier, J. Grandjean and P. Laszlo, *J. Am. Chem. Soc.*, **98** (1976) 3373.

[29] S.P. Dent, C. Eaborn and A. Pidcock, *J. Organomet. Chem.*, **97** (1975) 307.

[30] J.L. Spencer, *Inorg. Syntheses*, **19** (1979) 213.

[31] J.P. Birk, J. Halpern and A.L. Pickard, *J. Am. Chem. Soc.*, **90** (1968) 4491.

[32] P. Chini and G. Longoni, *J. Chem. Soc. A*, (1970) 1542.

[33] G. Vasapollo, L. Toniolo, G. Cavinato, F. Bigoli, M. Lanfranchi and M.A. Pellinghelli, *J. Organomet. Chem.*, **481** (1994) 173.

[34] J. Lewis, B.F.G. Johnson, K.A. Taylor and J.D. Jones, *J. Organomet. Chem.*, **32** (1971) C62.

[35] I. Omae, *Organometallic Intramolecular-coordination Compounds, J. Organometallic Chemistry Library 18*, Elsevier, Amsterdam, 1986.

[36] A.C. Cope and R.W. Siekman, *J. Am. Chem. Soc.*, **87** (1965) 3272.

[37] A.C. Cope and E.C. Friedrich, *J. Am. Chem. Soc.*, **90** (1968) 909.

[38] S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, **27** (1988) 2279.

[39] J. Terheijden, G. van Koten, D.M. Grove, K. Vrieze and A.L. Spek, *J. Chem. Soc. Dalton Trans.*, (1987) 1359.

[40] F. Balegroune, P. Braunstein, T.M.G. Carneiro, D. Grandjean and D. Matt, *J. Chem. Soc., Chem. Commun.*, (1989) 582.

[41] C.J. Mounlton and B.L. Shaw, *J. Chem. Soc. Dalton Trans.*, (1976) 1020.

[42] H.-P. Abicht, *J. Organomet. Chem.*, **311** (1986) 57.

[43] G.E. Hartwell, R.V. Lawrence and M.J. Smas, *J. Chem. Soc. Chem. Commun.*, (1970) 912.

[44] D.F. Gill, B.E. Mann and B.L. Shaw, *J. Chem. Soc. Dalton Trans.*, (1973) 270.

[45] C. Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J.H. Rodríquez-Ramos, J.R. Masaguer, J.L. García-Ruano and X. Solans, *Organometallics*, **12** (1993) 4104.

[46] S.D. Perera and B.L. Shaw, *J. Chem. Soc. Dalton Trans.*, (1995) 641.

[47] A.D. Ryabov and R. van Eldik, *Angew. Chem. Int. Ed. Engl.*, **33** (1994) 783.

[48] B.C. Ankianiec, V. Christou, D.T. Hardy, S.K. Thomson and G.B. Young, *J. Am. Chem. Soc.*, **116** (1994) 9963.

[49] S. Wimmer and F.L. Wimmer, *J. Chem. Soc. Dalton Trans.*, (1994) 879.

[50] G. Minghetti, M.A. Cinellu, S. Stoccoro, A. Zucca and M. Manassero, *J. Chem. Soc. Dalton Trans.*, (1995) 777.

[51] F. Gorla, L.M. Venanzi and A. Albinati, *Organometallics*, **13** (1994) 43.

[52] M.A. Bennett, H. Jin and A.C. Willis, *J. Organomet. Chem.*, **451** (1993) 249.

[53] F. Gorla, A. Togni, L.M. Venanzi, A. Albinati and F. Lianza, *Organometallics*, **13** (1994) 1607.

[54] A. Albinati, F. Lianza, P.S. Pregosin and B. Müller, *Inorg. Chem.*, **33** (1994) 2522.

[55] J. Terheijden, G. van Koten, J.A.M. van Beek, B.K. Vriesema, R.M. Kellogg, M.C. Zoutberg and C.S. Stam, *Organometallics*, **6** (1987) 89.

[56] P.R.R. Ranatunge-Bandarage, N.W. Duffy, S.M. Johnston, B.H. Robinson and J. Simpson, *Organometallics*, **13** (1994) 511.

[57] M.H. Rakowsky, J.C. Woolcock, L.L. Wright, D.B. Green, M.F. Rettig and R.W. Wing, *Organometallics*, **6** (1987) 1211.

[58] R. Bertani, A.M. Maccioni, P. Traldi and G. Carturan, *Inorg. Chim. Acta*, **121** (1986) 147.

[59] L. Chassot and A. von Zelewsky, *Inorg. Chem.*, **26** (1987) 2814.

[60] D. O'Hare, *Organometallics*, **6** (1987) 1766.

[61] M. Hackett and G.M. Whitesides, *Organometallics*, **6** (1987) 403.

[62] G.K. Anderson, R.J. Cross, S. Fallis and M. Rocamora, *Organometallics*, **6** (1987) 1440.

[63] D. O'Hare, *J. Organomet. Chem.*, **323** (1987) C13.

[64] A.C. Skapski, V.F. Sutcliffe and G.B. Young, *J. Chem. Soc. Chem. Commun.*, (1985) 609.

[65] P.R.R. Ranatunge-Bandarage, B.H. Robinson and J. Simpson, *Organometallics*, **13** (1994) 500.

[66] J. Terheijden, G. van Koten, F. Muller, D.M. Grove, K. Vrieze, E. Nielsen and C.H. Stam, *J. Organomet. Chem.*, **315** (1986) 401.

[67] M. Maestri, D. Sandrini, A. von Zelewsky and C. Deuschel-Cornioley, *Inorg. Chem.*, **30** (1991) 2476.

[68] E.W. Abel, D.G. Evans, J.R. Koe, V. Sik, P.A. Bates and M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, (1989) 985.

[69] F.M. Bickelhaupt, E.J. Baerends and W. Ravenek, *Inorg. Chem.*, **29** (1990) 350.

[70] C. Allevi, L. Garlaschelli, M.C. Malatesta and F. Ganazzoli, *J. Chem. Soc. Dalton Trans.*, (1988) 1949.

[71] C.A. Ghilardi, S. Midollini, S. Moneti and A. Orlandini, *J. Chem. Soc. Dalton Trans.*, (1988) 1833.

[72] D. Sandrini, M. Maestri, V. Balzani, L. Chassot and A. von Zelewsky, *J. Am. Chem. Soc.*, **109** (1987) 7720.

[73] R. Usón and J. Forniés, *Adv. Organomet. Chem.*, **28** (1988) 219.

[74] C. Allevi, R.D. Pergola, L. Garlaschelli, M.C. Malatesta, A. Albinati and F. Ganazzoli, *J. Chem. Soc. Dalton Trans.*, (1988) 17.

[75] B.L. Simms and J.A. Ibers, *J. Organomet. Chem.*, **327** (1987) 125.

[76] M. Crespo, M. Martinez and J. Sales, *Organometallics*, **12** (1993) 4297.

[77] A.D. Ryabov, L.G. Kuz'mina, V.A. Polyakov, G.M. Kazankov, E.S. Ryabova, M. Pfeffer and R. van Eldik, *J. Chem. Soc. Dalton Trans.*, (1995) 999.

[78] N.W. Duffy, C.J. McAdam, B.H. Robinson and J. Simpson, *Inorg. Chem.*, **33** (1994) 5343.

[79] A.J. Cheney, W.S. McDonald, K. O'Flynn, B.L. Shaw and B.L. Turtle, *J. Chem. Soc. Chem. Commun.*, (1973) 128.

[80] M. Crespo, X. Solans, M. Font-Bardía, *J. Organomet. Chem.*, **483** (1994) 187.

[81] E. Wehman, *Cyclometallated Complexes of Lithium, Copper and Platinum; A Study Concerning Their Synthesis and Properties (Thesis)*, 1988.

[82] J.A.M. van Beek, G. van Koten, W.J.J. Smeets and A.L. Spek, *J. Am. Chem. Soc.*, **108** (1986) 5010.

[83] I.C.M. Wehman-Ooyevaar, D.M. Grove, H. Kooijman, P. van der Sluis, A.L. Spek and G. van Koten, *J. Am. Chem. Soc.*, **114** (1992) 9916.

[84] G. van Koten, *Pure Appl. Chem.*, **61** (1989) 1681.

[85] V.I. Sokolov, *Inorg. Chim. Acta*, **18** (1976) L9.

[86] R. Mason, M. Textor, N. Al-Salem and B.L. Shaw, *J. Chem. Soc. Chem. Commun.*, (1976) 292.

[87] D.F. Gill and B.L. Shaw, *J. Chem. Soc. Chem. Commun.*, (1972) 65.

[88] R.J. Cross, A.R. Kennedy and K.W. Muir, *J. Organomet. Chem.*, **487** (1995) 227.

[89] M. Crespo, X. Solans and M. Font-Bardía, *Organometallics*, **14** (1995) 355.

[89a] M.M. Mdleleni, J.B. Bridgewater, R.J. Watts and P.C. Ford, *Inorg. Chem.*, **34** (1995) 2334.

[90] E.M. Badley, J. Chatt and R.L. Richards, *J. Chem. Soc. A*, (1971) 21.

[91] Y. Yamamoto and H. Yamazaki, *Coord. Chem. Rev.*, **8** (1972) 225.

[92] F.R. Hartley, *Inorg. Chim. Acta*, **5** (1971) 197.

[93] W.C. Zeisse, *Mag. Pharm.*, **35** (1830) 105.

[94] I. Yamamoto ed. *Yuki Kinzoku Kagoubutsu, Gosei-hou oyobi Riyo-hou*, Tokyo Kagaku Dojin, Tokyo, 1991.

[95] A.L. Rieger, G.B. Carpenter and P.H. Rieger, *Organometallics*, **12** (1993) 842.

[96] M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, *J. Chem. Soc. Chem. Commun.*, (1975) 449.

[97] M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, *J. Chem. Soc. Dalton Trans.*, (1977) 271.

[98] G. Ferguson, M. Parvez, P.K. Monaghan and R.J. Puddephatt, *J. Chem. Soc. Chem. Commun.*, (1983) 267.

[99] G.E. Herberich, U. Englert and F. Marken, *J. Chem. Soc. Dalton Trans.*, (1993) 1979.

[100] G. Booth and J. Chatt, *J. Chem. Soc. A*, (1966) 634.

[101] H. Jin and K.J. Cavell, *J. Chem. Soc. Dalton Trans.*, (1994) 415.

[102] S. Otsuka and K. Ataka, *J. Chem. Soc. Dalton Trans.*, (1976) 327.

[103] F. Faraone, L. Silvestro, S. Sergi and R. Pietropaolo, *J. Organomet. Chem.*, **34** (1972) C55.

[104] F. Faraone, L. Silvestro, S. Sergi and R. Pietropaolo, *J. Organomet. Chem.*, **46** (1972) 379.

[105] K. Onitsuka, K. Murakami, K. Matsukawa, K. Sonogashira, T. Adachi and T. Yoshida, *J. Organomet. Chem.*, **490** (1995) 117.

[106] J.-T. Chen, Y.-S. Yeh, C.-S. Yang, F.-Y. Tsai, G.-L. Huang, B.-C. Shu, T.-M. Huang, Y.-S. Chen, G.-H. Lee, M.-C. Cheng, C.-C. Wang and Y. Wang, *Organometallics*, **13** (1994) 4804.

[107] T.G. Appleton, H.C. Clark and L.E. Manzer, *J. Organomet. Chem.*, **65** (1974) 275.

[108] T.G. Appleton, M.A. Bennett, A. Singh and T. Yoshida, *J. Organomet. Chem.*, **154** (1978) 369.

[109] P.K. Monaghan and R.J. Puddephatt, *Organometallics*, **2** (1983) 1698.

[110] V.K. Jain, G.S. Rao and L. Jain, *Adv. Organomet. Chem.*, **27** (1987) 113.

[111] Z. Zhong, R.J. Hinkle, A.M. Arif and P.J. Stand, *J. Am. Chem. Soc.*, **113** (1991) 6196.

[112] R.J. Hinkle, P.J. Stang and A.M. Arif, *Organometallics*, **12** (1993) 3510.

[113] P.J. Stang, C.M. Crittell and A.M. Arif, *Organometallics*, **12** (1993) 4799.

[114] M.N.S. Hill, B.F.G. Johnson and J. Lewis, *J. Chem. Soc. A*, (1971) 2341.

[115] B.L. Shaw, *J. Chem. Soc. Chem. Commun.*, (1968) 464.

[116] W.A. Whitla, H.M. Powell and L.M. Venanzi, *J. Chem. Soc. Chem. Commun.*, (1966) 310.

[117] R. Palumbo, A.D. Renzi, A. Panunzi and G. Paiaro, *J. Am. Chem. Soc.*, **91** (1969) 3874.
[118] D.J. Cardin, B. Cetinkaya and M.F. Lappert, *Chem. Rev.*, **72** (1972) 545.
[119] E.M. Badley, J. Chatt and R.L. Richards, *J. Chem. Soc. A*, (1971) 21.
[120] L. Busetto, A. Palazzi, B. Crociani, U. Belluco, E.M. Badley, B.J.L. Kilby and R.L. Richards, *J. Chem. Soc. Dalton Trans.*, (1972) 1800.
[121] B. Cetinkaya, P. Dixneuf and M.F. Lappert, *J. Chem. Soc. Dalton Trans.*, (1974) 1827.
[122] R.L. Richards, *Inorg. Syntheses*, **19** (1979) 174.
[123] D.J. Cardin, B. Cetinkaya, E. Cetinkaya and M.F. Lappert, *J. Chem. Soc. Dalton Trans.*, (1973) 514.
[124] B. Cetinkaya, P. Dixneuf and M.F. Lappert, *J. Chem. Soc. Chem. Commun.*, (1973) 206.
[125] D.J. Cardin, B. Cetinkaya, E. Centinkaya, M.F. Lappert, L.J. Manojlovic-Muir and K.W. Muir, *J. Organomet. Chem.*, **44** (1972) C59.
[126] L. Manojlovic-Muir and K.W. Muir, *J. Chem. Soc. Dalton, Commun.*, (1974) 2427.
[127] E.M. Badley, J. Chatt, R.L. Richards and G.A. Sim, *J. Chem. Soc. Chem. Commun.*, (1969) 1322.
[128] B. Cetinkaya, M.F. Lappert and K. Turner, *J. Chem. Soc. Chem. Commun.*, (1972) 851.
[129] A.L. Balch, *J. Organomet. Chem.*, **37** (1972) C19.
[130] R. Walker and K.W. Muir, *J. Chem. Soc. Dalton Trans.*, (1975) 272.
[131] K.W. Muir, R. Walker, J. Chatt, R.L. Richards and G.H.D. Royston, *J. Organomet. Chem.*, **56** (1973) C30.
[132] L.M. Rendina, J.J. Vittal and R.J. Puddephatt, *Organometallics*, **14** (1995) 1030.
[133] B. Cetinkaya, E. Cetinkaya and M.F. Lappert, *J. Chem. Soc. Dalton Trans.*, (1973) 906.
[134] T.R. Lee and G.M. Whitesides, *Acc. Chem. Res.*, **25** (1992) 266.
[135] T.M. Miller, T.J. McCarthy and G.M. Whitesides, *J. Am. Chem. Soc.*, **110** (1988) 3156.
[136] T.M. Miller, A.N. Izumi, Y.-S. Shih and G.M. Whitesides, *J. Am. Chem. Soc.*, **110** (1988) 3146.
[137] T.M. Miller and G.M. Whitesides, *J. Am. Chem. Soc.*, **110** (1988) 3164.
[138] T.R. Lee and G.M. Whitesides, *J. Am. Chem. Soc.*, **113** (1991) 2576.
[139] T.R. Lee and G.M. Whitesides, *J. Am. Chem. Soc.*, **113** (1991) 2568.
[140] T.R. Lee and G.M. Whitesides, *J. Am. Chem. Soc.*, **113** (1991) 368.
[141] U. Matteoli, A. Scrivanti and S. Paganelli, *J. Organomet. Chem.*, **476** (1994) 145.
[142] A. Gusso, C. Baccin, F. Pinna and G. Strukul, *Organometallics*, **13** (1994) 3442.
[143] C. Baccin, A. Gusso, F. Pinna and G. Strukuk, *Organometallics*, **14** (1995) 1161.
[144] *Jikken Kagaku Kouza 25, 4th ed., Yuki Gosei, Yuki Kinzoku Shiyaku niyoru Gosei*, Japan Chem. Soc. ed., Maruzen, Tokyo, p. 428, 1991.
[145] J.L. Speier, J.A. Webster and G.H. Barnes, *J. Am. Chem. Soc.*, **79** (1957) 974.
[146] L.J. Kehoe and R.A. Schell, *J. Org. Chem.*, **35** (1970) 2846.
[147] R. Takeuchi, Y. Tsuji and Y. Watanabe, *J. Chem. Soc. Chem. Commun.*, (1986) 351.

22 Organocopper Compounds

22.1 INTRODUCTION

Recently organocopper compounds have been increasingly used for organosynthetic reactions. Reactions with copper metal or copper salt as catalysts, such as Ullmann reactions [1–7], Sandmeyer reactions and Gattermann reactions, are thought to occur via organocopper compounds as intermediates. However, researchers who study the organocopper compounds in itself as one of the studies of organometallic compounds, are relatively few. This chapter describes the use of organocopper compounds, laying stress on organosynthetic reactions.

22.2 COPPER

Copper belongs to group 11 in the periodic table and the outer electronic configuration is $3d^{10}4s^1$. Since the transition element is defined as an element of which d electrons do not completely fill its d orbital, copper does not simply belong to the transition elements because it has fully filled electrons in the d orbital. However, as copper is usually divalent and its d orbital is not full, copper can therefore be dealt with as a transition element since it shows the properties [8–11].

Copper exists as 50 ppm in the Earth's crust, and is the fifth element next to Fe, Ti, Al and Zn as the life span of metal resources (the life span of copper is 100 years or more). Therefore, copper is a metal which exists in relatively large amounts in the world. The production of copper was about 12 million tons in 1995 in the world [12–13b].

The ores of copper metal are native copper, oxide copper ores and sulfide copper ores, and the ores of copper metal in the world are largely sulfide copper ores. Copper ores become copper concentrate by flotation, and a matte is obtained by smelting, reverberating or autogenous smelting process. The smelting process is to separate metal sulfide as copper sulfide, iron sulfide and sulfur from a gangue smelting as shown in eq. (22.1) [14]. The smelting furnace process is the process of smelting the copper concentrate by burning it with coal and coke [14,15]. The reverberating furnace process is a process for smelting the ores by burning it with heavy oil and this process is the most widely used in the world because it is useful for treating powdered ores and for use in large productive capacity units. The autogenous smelting process is the process of smelting ores by burning the ores

$$2CuFeS_2 \longrightarrow Cu_2S + 2FeS + 1/2S_2 \qquad (22.1)$$

with sulfur without using any fuel. The mattes obtained by the smelting processes are transferred to a converter and are oxidized with air to separate a blister copper (Cu 98.7–98.9%) and a slag containing iron oxide. Highly pure copper (above 99.96%) is prepared by the electrorefinishing process of the blister copper [14].

The physical properties of copper are shown in Table 22.1. Copper has a higher electroconductivity and thermoconductivity than gold, next to those of silver. Copper is widely used in the electrical industry.

The inner 3d orbital of copper(I) is completely filled and the compounds of copper(I) are almost colorless. On the other hand, most copper(II) complexes are colored and paramagnetic as a result of the unpaired electron in the 3d orbital, and the copper has coordination numbers of 4 or 6 [16].

Copper in dry air at room temperature slowly develops a thin protective film of copper(I) oxide. On heating to high temperature in the presence of oxygen, copper first forms copper(I) oxide, then copper(II) oxide, both of which cover the metal as a loose scale. Copper has a high affinity to free halogen, molten sulfur, or hydrogen sulfide. Copper is essentially not attacked by nonoxidizing acids such as dilute sulfuric, hydrochloric, acetic, and other organic acids, and also is not attacked by alkali-metal hydroxide solutions. However, copper is soluble in oxidizing acids such as nitric acid, hot concentrated sulfuric acid, and chromic acid, or in non-oxidizing acids containing an oxidizing agent such as oxygen. For example, copper is dissolved in hydrochloric acid in the presence of oxygen. As fresh water has practically no corrosive effect on copper and seawater has only a small effect,

Table 22.1 Comparison of the physical properties of pure copper with those of silver and gold [16]

Property	Copper	Silver	Gold
atomic weight	63.546	107.87	196.97
melting point, °C	1083	960.8	1063
boiling point, °C	2595	2212	2970
density, kg/m^3	8.96×10^3	10.49×10^3	19.32×10^3
crystal structure	fcc†	fcc†	fcc†
ionic radius (M$^+$), nm	0.096	0.126	0.137
covalent radius, nm	0.138	0.153	0.150
electronegativity	2.43	2.30	2.88
1st ionization energy, J/mol	745×10^3	732×10^3	891×10^3
2nd ionization energy, J/mol	1950×10^3	2070×10^3	—
thermal conductivity, W/(m·K)	394	427	289
electrical resistivity 20 °C (Ω/cm)	1.6730	1.59	2.35
heat of fusion, J/kg	212×10^3	102×10^3	67.4×10^3
heat of vaporation, J/kg	7369×10^3	2400×10^3	1860×10^3
specific heat at 20 °C, J/kg/°C	384	233	131 (18 °C)
tensile strength, typical for annealed metal, kPa	23×10^4	28×10^4	17×10^4

† fcc = face-centered cubic structure

copper is used for marine materials. As copper has a high resistance to steam at high temperatures, it is used for materials for cooling device. Copper is used as a material for building construction, and in art and for ornaments [16,17,17a].

22.3 PREPARATION OF ORGANOCOPPER COMPOUNDS

Organocopper compounds are mainly prepared by the reaction of copper compounds with organolithium or with Grignard reagents as shown in eq. (22.2) [7,18–20]. The alkyl compounds of transition metals are very liable and it is very difficult

$$\mathrm{RM} + \mathrm{CuX} \longrightarrow \mathrm{RCu} + \mathrm{MX} \qquad (22.2)$$

$\mathrm{M = Li,\ MgX,\ 1/2Mg}$
$\mathrm{X = Cl,\ Br,\ I}$
$\mathrm{R = Me,\ Me_2C{=}CH,\ Ph,\ C_6H_4CH_2NMe_2\text{-}2,\ etc}$

to isolate them. However the methyl compound, which is not subjected to β-elimination, is relatively stable as shown in eq. (22.3). The methyl compound of a yellow solid is prepared by the reaction of CuI with MeLi or Me_2Mg in an ether solution [21]. MeCu decomposes to copper and ethane by heating in ether as shown in eq. (22.4).

$$\mathrm{CuI} + \mathrm{MeM} \xrightarrow[\text{in ether}]{-15\ ^\circ\mathrm{C}} \mathrm{MeCu} + \mathrm{MeI} \qquad (22.3)$$

$\mathrm{M = Li,\ 1/2Mg}$

$$\mathrm{MeCu} \longrightarrow 2\mathrm{Cu} + \mathrm{CH_3CH_3} \qquad (22.4)$$

When methyl copper is exposed to air, it explodes violently. Methyl copper does not dissolve in ether, but is able to dissolve in the ether which dissolved MeLi, and it forms Me_2CuLi as shown in eq. (22.5) [21]. Me_2CuLi is called the Gilmann

$$\mathrm{MeCu} + \mathrm{MeLi} \xrightarrow[\text{in ether}]{} \mathrm{Me_2CuLi} \qquad (22.5)$$

reagent which is widely used for organosynthetic reactions. House and co-workers [22] thought that the Gilmann reagent forms an ate complex ($Li^+Me_2Cu(OEt_2)_2^-$). Me_2CuLi is also called homocuprate since two organic groups are the same [23–25]. The compounds in which two bound organic groups are not the same are called mixed homocuprate, e.g., $Me(CH_2{=}CH)CuLi$. These compounds are prepared as follows: first, copper compounds with a more stable organic group than the other one are synthesized. Then they are reacted with the lithium compound having the other organic group as shown in eqs. (22.6)–(22.7) [26]. The compounds in which one organic group of the two bonds with a hetero atom are called heterocuprate (R(Z)CuM (Z=OR′, SR′, CN, Cl, Br), for example, MeCu(CN)Li, *t*-BuCu(SPh)Li, MeCu(CN)ZnI, *t*-BuCu(OPh)Li and PhCu(CN)Li. PhCu(CN)Li is prepared as follows; copper cyanide is suspended in anhydrous ether, an equimolar amount of the organic lithium compound is added to the ether solution and is stirred for three hours, as shown in eq. (22.8) [27].

$$\mathrm{CH_2{=}CHLi} \quad + \quad \mathrm{CuI} \xrightarrow[\text{in THF}]{-35\ ^\circ\mathrm{C}} \mathrm{CH_2{=}CHCu} \qquad (22.6)$$

$$\mathrm{CH_2{=}CHCu} \quad + \quad \mathrm{MeLi} \xrightarrow[\text{in THF}]{-35\ ^\circ\mathrm{C}} \mathrm{Me(CH_2{=}CH)CuLi} \qquad (22.7)$$

$$\mathrm{CuCN} \quad + \quad \mathrm{PhLi} \xrightarrow[\text{in ether}]{-\ 40^\circ\mathrm{C}} \mathrm{PhCu(CN)Li} \qquad (22.8)$$

Organocopper compounds become stable compounds by coordinating boron compounds or phosphines. Usually alkylcoppers besides methylcopper are difficult to synthesize due to the *β*-elimination described above. The complexes of boron compounds or phosphines are stable and they are widely used as reagents. For example, they are $BuCuBF_3$, $BuCuBEt_3$ and $MeCu(PPh_3)_2$ [25]. The $BuCuBF_3$ is synthesized as shown in eq. (22.9). At first, CuI is suspended in THF, and the suspension is added to the hexane solution of BuLi at −30 °C and on cooling at

$$\mathrm{BuLi} + \mathrm{CuI} \xrightarrow[\text{in THF}]{-30\ ^\circ\mathrm{C}} \mathrm{BuCu} \xrightarrow[\text{in THF}]{\mathrm{BF_3{\bullet}OEt_3},\ -70\ ^\circ\mathrm{C}} \mathrm{BuCuBF_3} \qquad (22.9)$$

−70 °C $BF_3{\cdot}OEt_2$ is added to the solution to afford the $BuCuBF_3$ [28]. In organocopper compounds, the example of utilization of RCu as organosynthetic reagents is few, and mainly homocuprate (R_2CuLi) such as Gilmann reagents are used. Further, mixed homocuprate (R^1R^2CuLi), heterocuprate (R(Z)CuM, Z=OR′. SR′, CN, Cl, Br) and organocopper–boron complexes used as high regio and stereoselective reagents are used as described below.

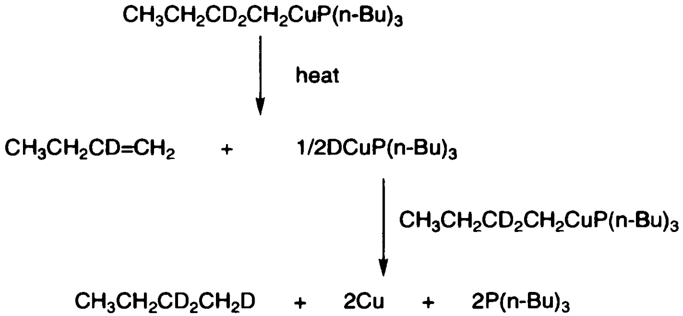
22.4 PROPERTIES OF ORGANOCOPPER COMPOUNDS

Alkyl coppers (RCu, R = alkyl) are usually liable and have explosive properties. The most stable methyl copper decomposes at −25 °C. Only a few examples of synthesis of higher alkyl coppers than methyl copper are known because of decomposition by β-elimination [29]. As described above, they are used as stable organosynthetic reagents by the coordination of boron compounds or phosphines.

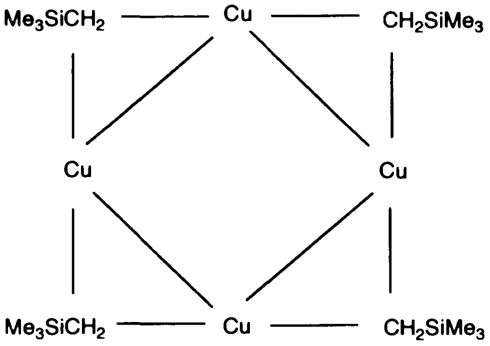
n-BuCuP(n-Bu)$_3$ decomposes completely at 0 °C for 4 h. The decomposition of the alkyl copper is not the radical decomposition of a Cu–C bond but the first stage is the formation of copper hydride by β-elimination, and the second stage is decomposition by reduction with copper hydride as shown in Scheme 22.1. This reaction mechanism is found by knowing that, when $CH_3CH_2CD_2CH_2CuP(n\text{-}Bu)_3$ is used as the organo copper compound, almost equimolar amounts of $CH_3CH_2CD{=}CH_2$ and $CH_3CH_2CD_2CH_2D$ are yielded as the decomposition products as shown in Scheme 22.1. But the decomposition of $CH_3CH_2CH_2CD_2CuP(n\text{-}Bu)_3$ forms $CH_3CH_2CH{=}CD_2$ [30].

Me_3SiCH_2Cu, in which the element at the β-position of the alkyl group is Si, is stable at room temperature and it decomposes at 78–79 °C. Its solubility is also improved, different from methyl copper. Then it dissolves in solvents such as benzene, cyclohexane and a light petroleum. It is colorless and forms a tetramer in benzene [31]. It dissolves in n-pentane, and is crystallized at −70 °C. The X-ray diffraction studies at −40 °C is shown in Figure 22.1 [32]. It has a square plane of copper atoms with the methylene carbons lying in the same pane and the methylene carbons form an electron-deficient bond in that one methylene carbon bonds to two copper atoms [32].

Phenyl copper is more stable than alkyl copper. Reiche synthesized PhCu as the first organocopper compounds in 1932 as shown in eq. (22.10) [16,18,33]. However, now it is considered that the obtained PhCu is not a pure product. Because, actually if we do not use less than the calculated amount of Grignard reagents, PhCu formed in the reaction shown in eq. (22.10) reacts with PhMgBr to afford the



Scheme 22.1 [30]



Cu-Cu : 2.417 Å
Cu-C (mean) : 2.02 Å
Cu-Cu-Cu . 89.8 °, 90.2 °

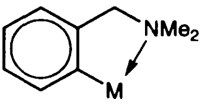
Figure 22.1 Crystal and molecular structure of $[CuCH_2SiMe_3]_4$ [32].

phenyl copper bonded with magnesium. For example, CuI reacts with two molar PhMgBr to afford $(PhCu)_2Ph_2Mg$ [33].

$$\mathrm{CuI} + \mathrm{PhMgBr} \xrightarrow[\text{in ether}]{} \mathrm{PhCu} + \mathrm{MgBrI} \qquad (22.10)$$

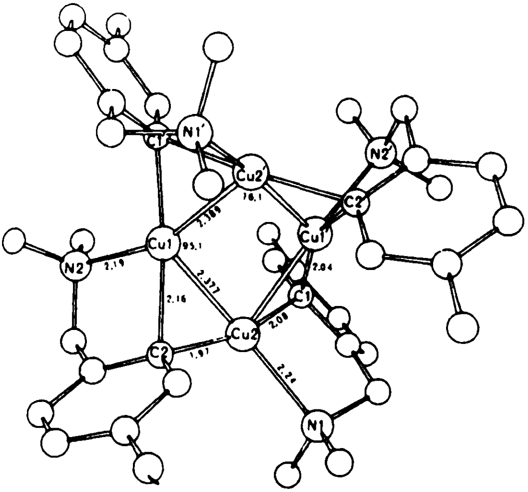
M = Li, 1/2Mg

(*o,m,p*)$CH_3C_6H_4Li$ react with CuBr to afford (*o,m,p*)$CH_3C_6H_4Cu$ almost quantitatively. (*o,m,p*)$CH_3C_6H_4Cu$ has almost the same stability to PhCu at 100–120 °C *in vacuo* and forms the dimer quantitatively [34]. 2-Dimethylaminomethylmetals are the representative compounds of organometallic intramolecular-coordination compounds. They form various kinds of five-membered ring compounds [35–38].



M = Si, Sn, Li, Hg, Mn, Ni, Cr, Co, Pt, Pd,
Rh, Ti, V, Sc, Y, La, Nd, Er, etc.

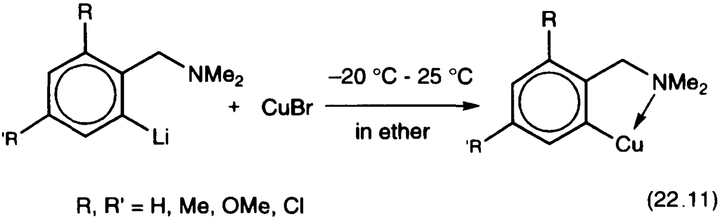
Organocopper compounds are also synthesized by the reaction shown in eq. (22.11) and these cyclic compounds are very stable compared with PhCu and $CH_3C_6H_4Cu$. For example, 2-[(dimethylamino)methyl][phenylcopper (R and $R' = H$ in eq. (22.11)) decomposes at 175–185 °C. These compounds are also stable



Cu-Cu : 2.38 Å
Cu-C (mean) : 2.06 Å

Figure 22.2 Structure of 5-methyl-2-[(dimethylaminomethyl)phenylcopper [40].

to hydrolysis and to oxygen [39]. The result of X-ray diffraction studies of 5-methyl-2-[(dimethylamino)methyl]phenylcopper (R = H, R′ = Me in eq. (22.11)) is shown in Figure 22.2 and the compound forms a tetranuclear cluster [40]. The four copper atoms are positioned in a butterfly arrangement, intermediate between a square planar and a tetrahedral situation. One carbon of the benzene ring bonds to two copper atoms, that is, it forms an electron-deficient bond, and the plane of the phenyl ring is orientated almost perpendicular to the Cu–Cu axis [40]. It forms the five-membered ring structure by the coordination of nitrogen atoms to the copper atom [40].



(22.11)

If an alkyl group or an aryl group bonds with a halogen, the organocopper compounds have much improved stability due to the stabilizing action of the halogen atom. In particular, the fluoro compounds are very stable [41]. For example, pentafluorophenylcopper decomposes above 200 °C. The solubility to organic solvents is high [42].

Generally, the order of the stability of organocopper compounds is as follows:

$$\text{alkyl} < \text{alkenyl} < \text{aryl} < \text{alkynyl}$$

In particular, acetylenyl copper is very stable. For example, Cu acetylide is a polymeric compound, and decomposes above 200 °C [18].

22.5 APPLICATIONS OF ORGANOCOPPER COMPOUNDS

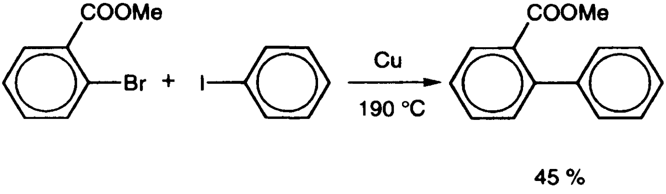
Organocopper compounds have not been industrially developed on a large scale as done for organosilicon or organotin compounds. However, recently they have been noted as reagents for organic synthesis and many reviews and books have been published [25,26,43–59]. The author will describe organosynthetic reactions with copper metal or copper salts as catalysts before he describes applications of the organosynthetic reactions of organocopper compounds, for it is thought that organocopper compounds act as the active species in these reactions. But, as organocopper compounds are largely very liable, it is difficult to support clearly the action of organocopper compounds as the intermediate at high temperatures. For example, a copper powder is used for the production of dimethyldichlorosilane at 250–300 °C by the reaction of methyl chloride with metallic silicon. Since the stream of methyl chloride at 300 °C will remove the copper from a copper mirror on glass and redeposit the copper downstream, it is believed that the reaction proceeds via the formation of methyl copper and decomposition of methyl copper to copper and a methyl group [60]. The most famous organosynthetic reaction with metallic copper or a copper salt is the Ullmann synthesis [1–6,43]. There are two kinds of synthetic reactions in this. One is that a diaryl is synthesized by the condensation of two moles of aryl halides as shown in eq. (22.13).

$$\mathrm{MeCl} \quad + \quad \mathrm{Si} \xrightarrow[250\text{ - }300\ ^\circ\mathrm{C}]{\mathrm{Cu}} \mathrm{Me_2SiCl_2} \qquad (22.12)$$

$$\mathrm{ArX} \quad + \quad \mathrm{A'rX} \xrightarrow[100\text{ - }300\ ^\circ\mathrm{C}]{\mathrm{Cu}} \mathrm{Ar{-}A'r} \quad + \quad \mathrm{CuX_2} \qquad (22.13)$$

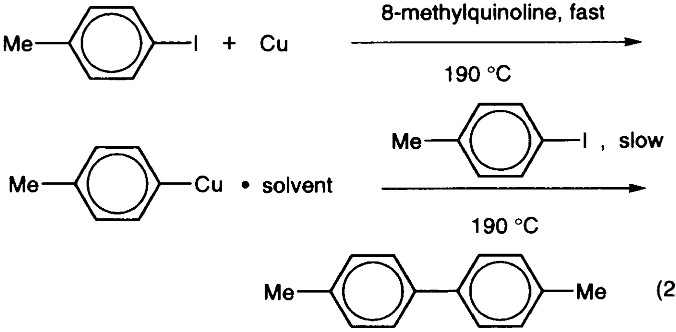
For example, the synthesis of biphenylester shown in eq. (22.14). The order of reactivity of aryl halides is as follows:

$$\mathrm{ArI} > \mathrm{ArBr} > \mathrm{ArCl}$$



(22.14)

The iodide is the most reactive [43]. As shown in eq. (22.15), *p*-iodetoluene reacts in 8-methylquinoline (bp 247.3–248.3 °C/751 mmHg) as a solvent and the formation of a *p*-tolylcopper complex coordinated by the solvent as intermediate is found by measurement of the amounts of raw material and product over the course of time. Namely, *p*-iodetoluene is completely consumed in 95 h, but the product 4,4-dimethylbiphenyl continues to form from the copper complex intermediate for 285 h after that [2,61].

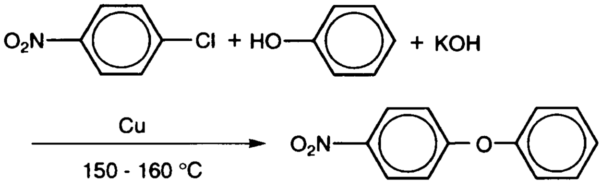


(22-15)

The formation of organocopper intermediate in the Ullmann reaction is thought to result from the following [2,61]:

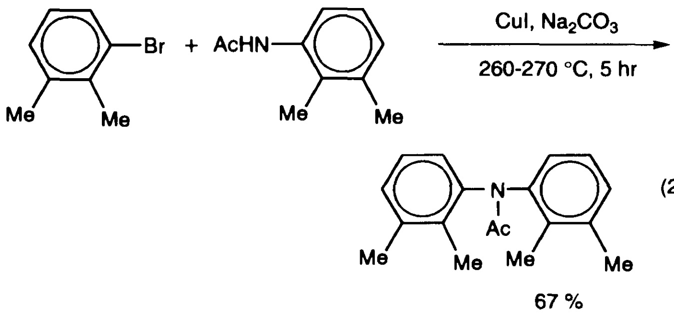
(1) The formation of asymmetric diaryl compounds easily proceeds as shown in eq. (22.14)
(2) Actually diaryl compounds are obtained by the reaction of arylcopper compounds with aryl halides.
(3) Diaryl compounds are obtained together with the formation of a copper mirror from the reaction solution.

Another Ullmann synthesis is the syntheses of arylethers or diarylamines by the condensation reactions of aryl halides with phenols or arylamines. For example, reactions are shown in eqs. (22.16) [62] and (22.17) [63], and especially the former reaction is used for the production of polyphenylether type heat-resistant synthetic lubricants.



(22.16)

260-270 °C, 5 hr



(22.17)

Copper tends to form more stable organocopper compounds with acetylene compounds than with aryl compounds. The synthetic reaction of acetylenic compounds with copper or copper salt, e.g., the Cadiot–Chodkiewics and Glaser reactions are well known. The Cadiot–Chodkiewics reaction is a reaction where 1-bromoalkyne easily reacts with a terminal alkyne in the presence of a catalytic amount of a cuprous salt or amines to afford conjugate diacetylene compounds in high yield [43]. For example, polyacetylene is easily synthesized as shown in eq. (22.19) [43].

$$\mathrm{RC{\equiv}CH + BrC{\equiv}CR'} \xrightarrow[\text{base}]{\text{Cu(I)}} \mathrm{RC{\equiv}C\text{-}C{\equiv}C\text{-}R' + Cu^{+} + H^{+}} \qquad (22.18)$$

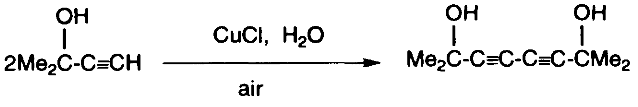
$$\mathrm{MeC{\equiv}C\text{-}C{\equiv}CH + BrC{\equiv}C\text{-}CH{=}CH\text{-}CH_2OH} \xrightarrow[\text{in THF, MeOH}]{\text{CuCl, EtNH}_2}$$

$$\mathrm{MeC{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH{=}CHCH_2OH} \qquad (22.19)$$

95 %

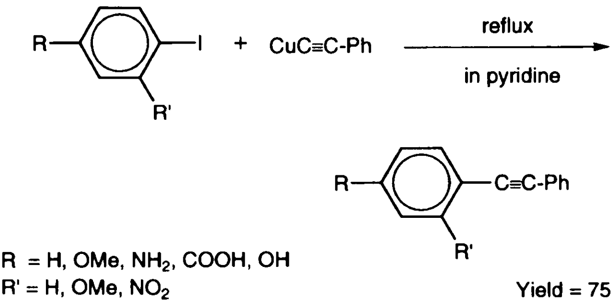
The Glaser reaction is a reaction to synthesize a conjugate diyne by an oxidative coupling reaction in the presence of a catalytic amount of copper salt. For example, a diyne is quantitatively obtained by the reaction in the presence of air as shown in eq. (22.21) [43].

$$\mathrm{2R\text{-}C{\equiv}CH + [O]} \xrightarrow{\text{Cu(I)}} \mathrm{R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}R} \qquad (22.20)$$

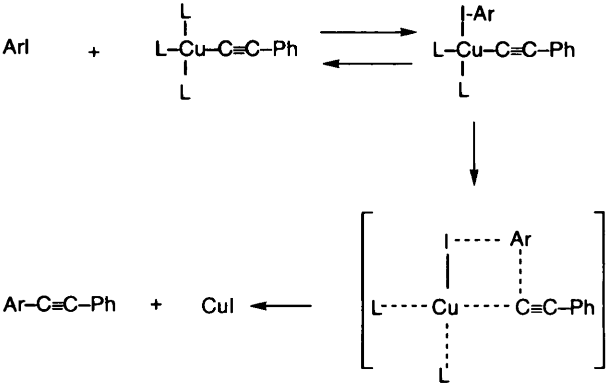


$$\mathrm{2Me_2\overset{\overset{\displaystyle OH}{|}}{C}\text{-}C{\equiv}CH} \xrightarrow[\text{air}]{\text{CuCl, H}_2\text{O}} \mathrm{Me_2\overset{\overset{\displaystyle OH}{|}}{C}\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}\overset{\overset{\displaystyle OH}{|}}{C}Me_2} \qquad (22.21)$$

The Cadiot–Chodkiewcz and Glaser reactions are the synthetic reaction with acetylene type compounds. As the acetylene compounds easily form stable organocopper compounds, these acetylenecopper compounds react directly with halides to afford the acetylene derivatives. This synthetic reaction is called the Castro reaction [43]. For example, as shown in eq. (22.22), aryl compounds having functional groups such as OMe, NO_2 and COOH are able to condense with copper acetylides [64]. The Castro reaction as shown in eq. (22.22), is thought to proceed through a four-center reaction mechanism as shown in Scheme 22.2 [64]. If the compound has a hetero atom at the ortho position, the cyclization proceeds to afford the heteroalkenyl compound in the Castro reaction as shown in eq. (22.23) [43,64,65]. For example, isocoumarin, benzofuran and indole are synthesized respectively regarding the kinds of XH in eq. (22.23) [64,65].

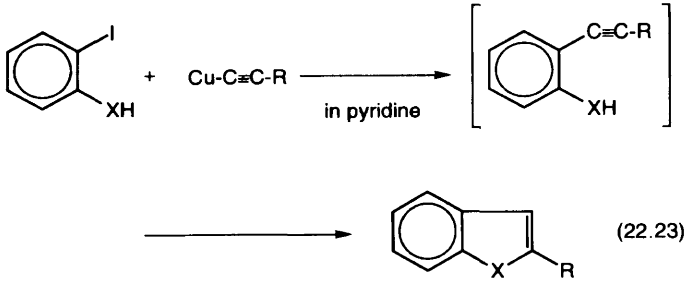


(22.22)

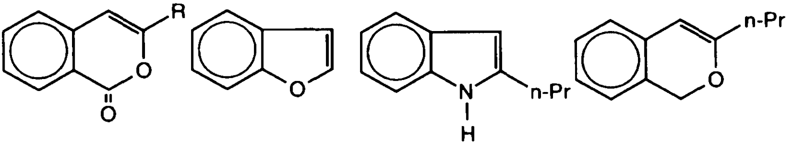


L = pyridine

Scheme 22.2 [66]



(22.23)



XH = COOH
P = Ph
Yield = 91 %

XH = OH
P = Ph
Yield = 88 %

XH = NH_2
P = n-Pr
Yield = 85 %

XH = CH_2OH
P = n-Pr
Yield = 50 %

The Castro reaction with acid halides as the halide affords the ketone as shown in eq. (22.24) [66]. The Castro reaction is a condensation reaction between acetylene copper and halides as shown in eqs. (22.22)–(22.24).

$$\mathrm{RCOCl} + \mathrm{R'C{\equiv}CCu} \longrightarrow \underset{80\text{-}95.5\ \%}{\mathrm{RCOC{\equiv}CR'}} \qquad (22.24)$$

R = CH_3, C_4H_9, CH_2=CH, C_6H_5
R'= C_4H_9, C_5H_{11}, C_6H_5

Alkylcoppers, arylcoppers, allylcoppers and vinylcoppers, besides acetylenecoppers, are also able to be used as organocopper reagents. The reactions with organocopper compounds, besides acetylene coppers, are not called the Castro reaction. However, recently these reactions are noted as being highly selective [43–69].

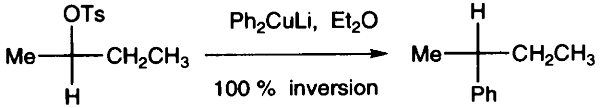
The organocopper compounds react mainly with halides and they also react with aryl compounds, acetals, tosylates ($R\text{-}OSO_2\text{-}C_6H_4CH_3(\text{-}p)$) and tolyflates ($R\text{-}OSO_2CF_3$). The reactions with halides are first order to each of the concentrations and they are S_N2 reactions. The order of reactivity of alkyl halides regarding the alkyl group is as follows:

$$\text{primary} > \text{secondary} \gg \text{tertiary},$$

and the order of the reactivity of halides is

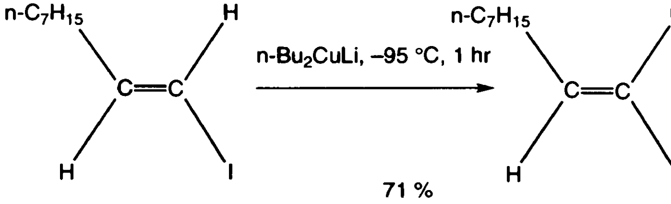
$$\text{iodides} > \text{bromides} > \text{chlorides [67].}$$

In the reaction of alkyl halides or alkyltosylate, etc. the reaction proceeds with an inversion in the stereochemistry [68]. The reaction of vinyl halides or alkenyl halides bonded with halogen at the vinyl group retains the stereochemistry as shown in eq. (22.26) [69,70]. In the reaction with allyl halides, S_N2 reaction (the usual two molecular nucleophilic substitution reaction) and the S_N2' reaction on allyl rearrangement proceed simultaneously by organocopper reagents as shown in eq. (22.27) [55].

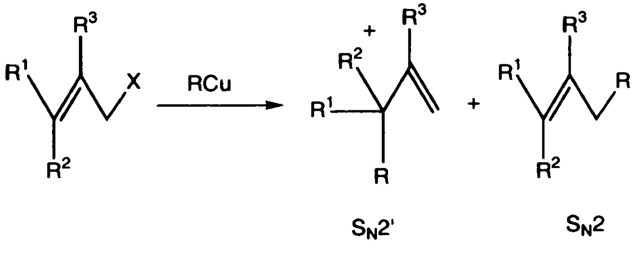


$$\begin{array}{c}\text{OTs}\\ \text{Me}-\!\!+\!\!-\text{CH}_2\text{CH}_3\\ \text{H}\end{array} \xrightarrow[\text{100 \% inversion}]{\text{Ph}_2\text{CuLi, Et}_2\text{O}} \begin{array}{c}\text{H}\\ \text{Me}-\!\!+\!\!-\text{CH}_2\text{CH}_3\\ \text{Ph}\end{array} \qquad (22.25)$$

Ts = p-toluenesulfonyl, p-CH_3-C_6H_4-SO_2-

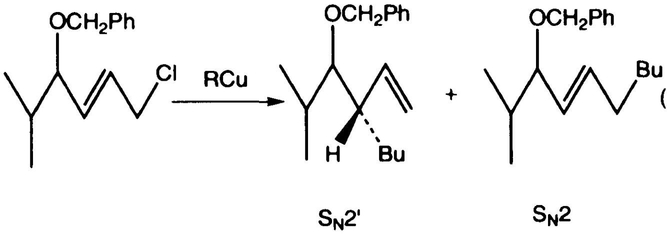


(22.26)



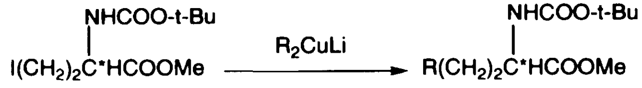
(22.27)

For example, as shown in eq. (22.28), the S_N2 product is obtained in 88% yield with Bu_2CuLi as the organocopper reagent. On the other hand, the S_N2' product is obtained in 98% yield with $Bu_2CuZnCl$, $Bu_2CuTi(O\text{-}i\text{-}Pr)_3$ or $BuCuBF_3$ as the organocopper reagent [71]. As the nucleophilicity of organocopper compounds is smaller than that of Grignard reagents or organolithium compounds, organocopper compounds do not react with the carbonyl group of ketones or esters. Therefore the organocopper compounds are able to selectively react with halides. For example, an aminoester is directly alkylated with the organocopper compound to afford the product in excellent ee% yield as shown in eq. (22.29) [72,73].



(22.28)

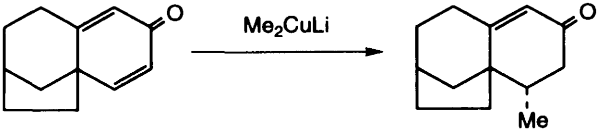
RCu = Bu_2CuLi, $Bu_2CuZnCl$
$Bu_2CuTi(O\text{-}iPr)_3$, $BuCuBF_3$



$$\overset{\text{NHCOO-t-Bu}}{I(CH_2)_2C^{*}HCOOMe} \xrightarrow{R_2CuLi} \overset{\text{NHCOO-t-Bu}}{R(CH_2)_2C^{*}HCOOMe} \quad (22.29)$$

R = Et 87 % (>95 % ee)
R = n-Bu 89 % (>95 % ee)

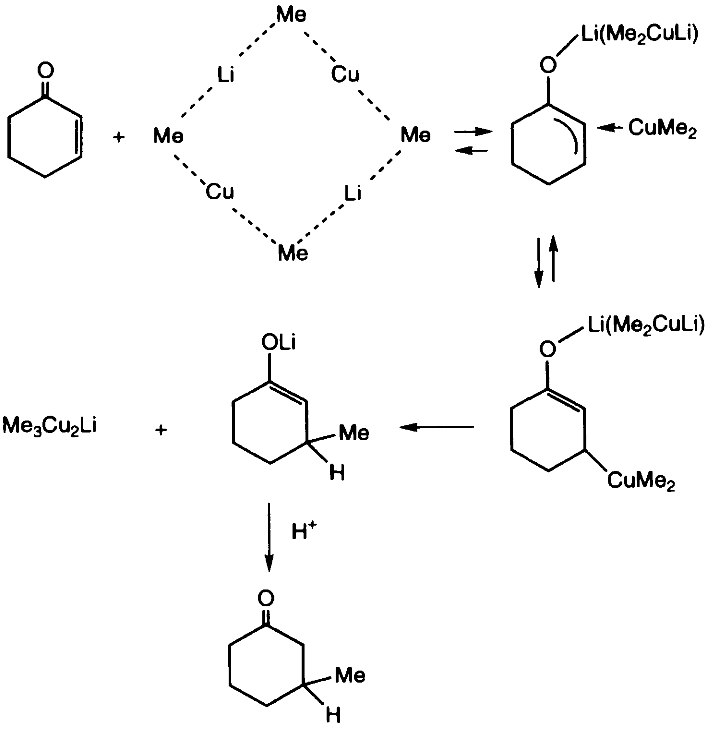
The representative reaction with organocopper compounds is an addition reaction to an α,β-unsaturated carbonyl group. As the nucleophilicity of the organocopper compounds is smaller than that of Grignard reagents or organolithium compounds as described above, they are able to perform 1,4-addition reaction to double bonds conjugated with the carbonyl groups of ketones and esters. For example, Me_2CuLi reacts with dienone to afford 1,4-addition product in 96% yield as shown in eq. (22.30) [74–76].



(22.30)

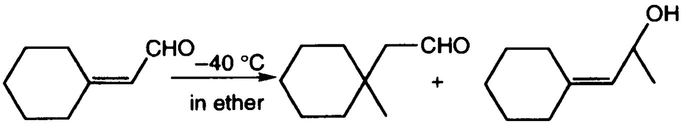
96 %

Corey and co-workers [77] have presumed Scheme 22.3 for the 1,4-addition of organocopper compounds of the Gilmann reagent (Me_2CuLi) with the simplest α,β-unsaturated ketone. The reaction proceeds via an intermediate state in that the copper is coordinated with the unsaturated bond and the lithium bonds to the oxygen of the carbonyl group. The 1,4-addition reactivity of conjugated ketones is higher than that of the conjugated esters. The reactivity diminishes greatly when bulky substituents bond near the double bond. Organocopper compounds do not perform a 1,4-addition reaction to conjugated carboxylic acids or conjugated amides. The reactivity of conjugated aldehyde is high and in the reaction of homocuprate, both 1,2-addition and 1,4-addition reactions proceed [25]. For example, the reaction of the α,β-unsaturated aldehyde affords a mixture of β-



Scheme 22.3 [78]

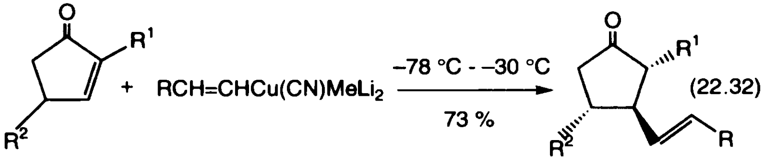
methyl aldehyde by 1,4-addition and allylalcohol by 1,2-addition as shown in eq. (22.31) [78,79].



(22.31)

	Yield			
Me$_2$CuLi	71 %	87.0	:	13.0
Me$_5$Cu$_3$Li$_2$	90 %	99.0	:	1.0

As organocopper compounds show the high selectively of 1,4-addition shown in eq. (22.30), these reactions are applied to the synthesis of pharmaceuticals such as prostaglandins shown in eq. (22.32) [80].

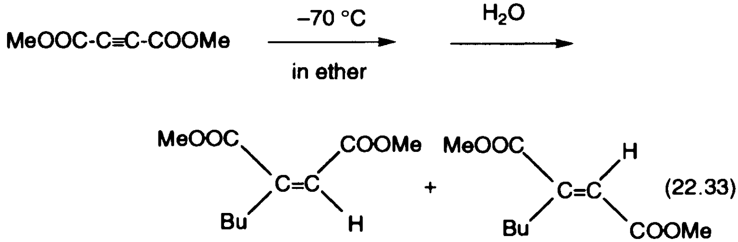


(22.32)

misoprostol

$R^1 = (CH_2)_6COOMe$
$R^2 = OSiMe_3$
$R = CH_2C(Me)(OSiMe_3)(n\text{-}Bu)$

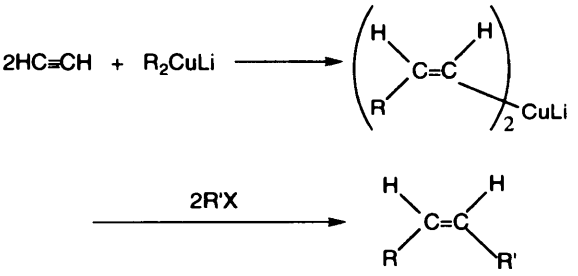
The 1,4-addition of α,β-unsaturated carbonyl proceeds not only to the double bond but also to the triple bond of unsaturated carbonyl compounds. For example, a *cis*-alkene is selectively obtained with an organocopper boron compound as shown in eq. (22.33) [81].



(22.33)

	Yield			
n-BuCuB(n-Bu)$_3$	93 %	>99	:	<1
nBuCuBF$_3$	85 %	87	:	13
n-Bu$_2$CuLi	98 %	60	:	40

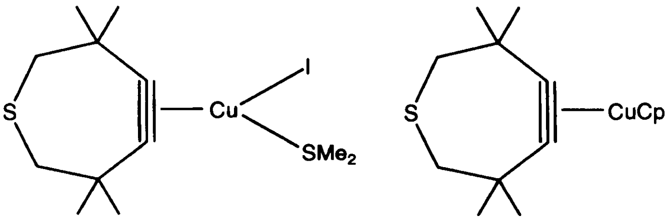
Organocopper compounds make *cis*-addition to a simple acetylene to afford the alkenylcopper compounds and further they react with organic halides to afford *cis*-alkenes by a coupling reaction as shown in eq. (22.34) [82–85].



(22.34)

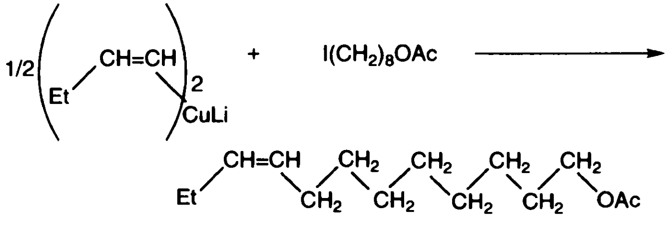
$R = Et, n\text{-}Bu, n\text{-}C_5H_{11}, n\text{-}C_7H_{15}$, etc.
$R'X = H_2C{=}CHCH_2I, CH_3CH{=}CHCH_2Br, H_3C\text{-}O\text{-}CH_2Cl$, etc.

Recently, in *ab initio* theoretical studies of the addition of MeCu to acetylenes, the reaction mechanism of a *cis*-addition has been reported as shown in Scheme 22.4. The addition is a highly exothermic reaction, by 37.7 kcal/mol [86]. On the other hand, recently, the X-ray diffraction studies of π-bonds of acetylene–copper have been reported as follows [87,88]:



Cu–C$_1$	1.913 Å	1.954 Å
Cu–C$_2$	1.951 Å	1.937 Å
C≡C	1.227 Å	1.236 Å

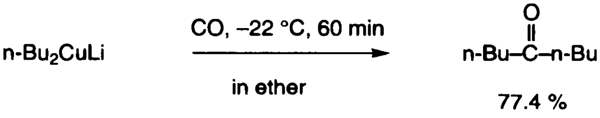
The alkylation of Z dialkenylcopper is applied to the synthesis of an insect sex pheromone as shown in eq. (22.35) [83].



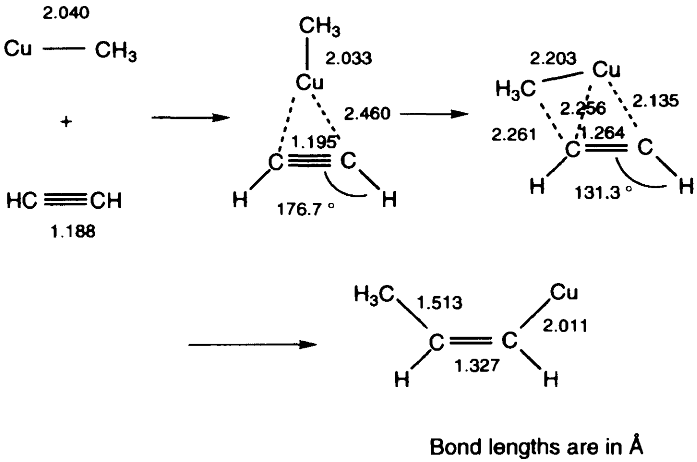
(22.35)

Yield = 81 %
Z purity = 99.9 %

In organocopper compounds, an insertion reaction proceeds on carbon monoxide, isonitrile and carbon dioxide [58]. For example, carbon monoxide inserts into organocopper compounds to afford the ketone as shown in eq. (22.36) [89]. The 1,4-addition of organocopper compounds proceeds on the conjugate carbonyl compounds as shown in eq. (22.31), described above. On the other hand, a 1,2-addition proceeds stereospecifically on non-conjugated aldehydes or ketones [54,90].



$$n\text{-}Bu_2CuLi \xrightarrow[\text{in ether}]{\text{CO, }-22\ ^\circ\text{C, 60 min}} \underset{77.4\ \%}{n\text{-}Bu\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}n\text{-}Bu} \qquad (22.36)$$



Scheme 22.4 [86]

REFERENCES

[1] P.E. Fanta, *Chem. Rev.*, **64** (1964) 613.
[2] P.E. Fanta, *Synthesis*, (1974) 9.
[3] T. Cohen and I. Cristea, *J. Org. Chem.*, **40** (1975) 3649.
[4] T. Cohne and J.G. Tirpak, *Tetrahedron Lett.*, (1975) 143.
[5] R.C. Fuson and E.A. Cleveland, *Org. Synthesis*, Col. vol. 3. p. 339, (1955).
[6] T. Cohen and I. Cristea, *J. Am. Chem. Soc.*, **98** (1976) 748.
[7] J.E. Gowan and T.S. Weeler, *Name Index of Organic Reaction*, Longmans, London, 1960.
[8] Ch. Elschenbroich and A. Saltzer, *Organometallics*, VCH, Weinheim, 1989.
[9] E.G. Rochow, D.T. Hurd and R.N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley, New York, 1957.
[10] C.M. Lukehart, *Fundamental Transition Metal Organometallic Chemistry*, Brooks/Cole, Monterey, 1985.
[11] H. Yamazaki and Y. Wakatsuki, *Yuki Kinzoku no Kagaku (Organometallic Chemistry)*, Japan Chemical Society, Dai Nippon Tosho, Tokyo, 1989.
[12] *Titan no Sekai*, Japan Titanium Society, 1991.
H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
[13] *1987 Statistical Yearbook*, Thirty-sixth issue, Department of International Economic and Social Affairs, Statistical Office, United Nations, New York, 1990.
[13a] T. Imai, *Kagaku Keizai*, April (1994) 55.
[13b] *Kogyo, Biran*, Tsusho Sangyo Chosakai Shuppanbu, 1997.
[14] *Kagaku Binran Ooyohen*, Japan Chemical Society, Maruzen, Tokyo, 1980.
[15] *11691 no Kagaku Shohin*, Kagaku Kogyo Nipposha, p. 103, 1991.
[16] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed. John Wiley, New York, vol. 6, p. 819, 1980.
[17] *Kagaku Daijiten*, Tokyo Kagaku Dojin, p. 1557, 1989.
[17a] *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., VCH, Weinheim, vol. A7, p. 471, 1986.

[18] G. van Koten and J.G. Noltes, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 2, p. 709, 1982.
[19] A.E. Jukes, *Adv. Organomet. Chem.*, **12** (1974) 215.
[20] *Methoden der Organishen Chemie*, Houben-Weyl, Band XIII/1, p. 735, 1970.
[21] H. Gilman, R.G. Jones and L.A. Woods, *J. Org. Chem.*, **17** (1952) 1630.
[22] H.O. House, W.L. Respess and G.M. Whitesides, *J. Org. Chem.*, **31** (1966) 3128.
[23] G.H. Posner, *An Introduction to Synthesis Using Organocopper Reagents*, John Wiley, New York, 1980.
[24] Y. Yamamoto and Y. Naruta, *Yuki Kinzoku Kagaku (Organometallic Chemistry)*, Maruzen, Tokyo, p. 157, 1983.
[25] H. Ozawa, *Yuki Kinzoku Kagoubutsu, Goseiho oyobi Riyoho (Syntheses and Applications of Organometallic Compounds)*, A. Yamamoto, ed., Tokyo Kagaku Dojin, Tokyo, p. 251, 1991.
[26] G.H. Posner, J.J. Sterling, C.E. Whitten, C.M. Lentz and D.J. Brunelle, *J. Am. Chem. Soc.*, **97** (1975) 107.
[27] J.P. Marino and N. Hatanaka, *J. Org. Chem.*, **44** (1979) 4467.
[28] K. Maruyama and Y. Yamamoto, *J. Am. Chem. Soc.*, **99** (1977) 8068.
[29] K.-H. Thiele and J. Köhler. Stedronsky, C.P. Casey and J.S. Filippo, Jr., *J. Am. Chem. Soc.*, **92** (1970) 1426.
[30] G.M. Whitesides, E.R. Stedronsky, C.D. Casy and J.S. Filippo, Jr, *J. Am. Chem. Soc.*, **92** (1970) 1426.
[31] M.F. Lappert and R. Pearce, *J. Chem. Soc., Chem. Commun.*, (1973) 24.
[32] J.A.J. Jarvis, R. Pearce and M.F. Lappert, *J. Chem. Soc. Dalton Trans.*, (1977) 999.
[33] G. Costa, A. Camus, L. Gatti and M. Marsich, *J. Organomet. Chem.*, **5** (1966) 568.
[34] A. Camus and N. Marsich, *J. Organomet. Chem.*, **14** (1968) 441.
[35] I. Omae, *Organometallic Intramolecular-coordination Compounds*, *J. Organomet. Chem. Library 18*, Elsevier, Amsterdam, 1986.
[36] I. Omae, *Chem. Rev.*, **79** (1979) 287.
[37] I. Omae, *Yuki Gosei Kagaku Kyokaishi*, **40** (1982) 147.
[38] I. Omae, *Coord. Chem. Rev.*, **83** (1988) 137.
[39] G. van Koten, A.J. Leusink and J.G. Noltes, *J. Organomet. Chem.*, **84** (1975) 117.
[40] G. van Koten and J.G. Noltes, *J. Organomet. Chem.*, **84** (1975) 129.
[41] A. Camus, N. Marsich, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, **23** (1977) 131.
[42] A. Cairncross and W.A. Sheppard, *J. Am. Chem. Soc.*, **90** (1968) 2186.
[43] W. Carruthers, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel ed., Pergamon Press, Oxford, vol. 7, p. 661, 1982.
[44] J.F. Normant, *Synthesis*, (1972) 63.
[45] Y. Yamamoto, *Angew. Chem. Int. Ed. Engl.*, **25** (1986) 947.
[46] C. Ullenius and B. Christenson, *Pure Appl. Chem.*, **60** (1988) 57.
[47] K.F. Normant and A. Alexakis, *Synthesis*, (1981) 841.
[48] J.F. Normant, *Pure Appl. Chem.*, **50** (1978) 709.
[49] G. van Koten, *J. Organomet. Chem.*, **400** (1990) 283.
[50] G.H. Posner, *Organic Reactions*, **19** (1972) 1.
[51] G.H. Posner, *Organic Reactions*, **22** (1975) 253.
[52] G.H. Posner, *An Introduction to Synthesis using Organocopper Reactions*, John Wiley, New York, 1980.
[53] T. Miki, Y. Ito and M. Kumada, *Yuki Kinzoku Kagobutsu omochiiru Gosei Hanno II (Organic Synthesis Using Organometallic Compounds II)*, Maruzen, Tokyo, p. 1, 1975.
[54] R.J.K. Taylor, *Synthesis*, (1985) 364.
[55] E. Nakamura and M. Isaka, *Yuki Gosei Kagaku Kyokaishi*, **49** (1991) 902.
[56] Y. Yamamoto, H. Nemoto and T. Ibuka, *Yukagaku*, **39** (1990) 881.

[57] Y. Yamamoto, *Yuki Gosei Kagaku Kyokaishi*, **44** (1986) 829.

[58] R. Noyori, *Yuki Gosei Kagaku Kyokaishi*, **34** (1976) 675.

[59] Y. Ito, *Yuki Gosei Kagaku Kyokaishi*, **37** (1979) 991.

[60] E.G. Rochow, D.T. Hurd and R.N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley, New York, p. 252, 1957.

[61] A.H. Lewin and T. Cohen, *Tetrahedron Lett.*, (1965) 4531.

[62] R.Q. Brewster and T. Groening, *Org. Syntheses*, Col. vol. 2, p. 445, 1957.

[63] W. Carruthers, *J. Chem. Soc. C*, (1968) 2244.

[64] R.D. Stephens and C.E. Castro, *J. Org. Chem.*, **28** (1963) 3313.

[65] C.E. Castro, R. Havlin, V.K. Honwad, A. Malte and S. Moje, *J. Am. Chem. Soc.*, **91** (1969) 6464.

[66] J.F. Normant and M. Bourgain, *Tetrahedron Lett.*, (1970) 2659.

[67] A. Yamamoto, *Yuki Kinzoku Kagaku, Kiso to Ooyo*, Shokabo, p. 341, 1982.

[68] C.R. Johnson and G.A. Dutra, *J. Am. Chem. Soc.*, **95** (1973) 7783.

[69] E.J. Corey and G.H. Posner, *J. Am. Chem. Soc.*, **89** (1967) 3911.

[70] E.J. Corey and G.H. Posner, *J. Am. Chem. Soc.*, **90** (1965) 5615.

[71] E. Nakamura, K. Sekiya, M. Arai and S. Aoki, *J. Am. Chem. Soc.*, **111** (1989) 3091.

[72] A. Bernardini, A. El Hallaoui, R. Jacquier, Ch. Pigiere, Ph. Viallefont and J. Bajgrowicz, *Tetrahedron Lett.*, (1983) 3717.

[73] J.A. Bajgrowicz, A. El Hallaoui, R. Jacquier, Ch. Pigiere and Ph. Viallefont, *Tetrahedron Lett.*, (1984) 2231.

[74] J.A. Marshall and S.F. Brady, *Tetrahedron Lett.*, (1969) 1387.

[75] J.A. Marshall and S.F. Brady, *J. Org. Chem.*, **35** (1970) 4068.

[76] J. Westermann and K. Nichisch, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 1368.

[77] E.J. Corey and F.J. Hannon, *Tetrahedron Lett.*, (1990) 1393.

[78] D.L.J. Clive, V. Farina and P.L. Beaulieu, *J. Org. Chem.*, **47** (1982) 2572.

[79] D.L.J. Clive, V. Farina and P.L. Beaulieu, *J. Chem. Soc. Chem. Commun.*, (1981) 643.

[80] K.A. Babiak, J.R. Behling, J.H. Dygos, K.T. McLaughlin, J.S. Ng, V.J. Kalish, S.W. Kramer and R.L. Shone, *J. Am. Chem. Soc.*, **112** (1990) 7441.

[81] Y. Yamamoto, H. Yatagai and K. Maruyama, *J. Org. Chem.*, **44** (1979) 1744.

[82] A. Alexakis, G. Cahiez and J.F. Normant, *Synthesis*, (1979) 826.

[83] G. Cahiez, A. Alexakis and J.F. Normant, *Tetrahedron Lett.*, (1980) 1433.

[84] M. Furber, R.J.K. Taylor and S.C. Burford, *J. Chem. Soc. Perkin Trans.*, (1986) 1809.

[85] N. Jabri, A. Alexakis and J.F. Normant, *Tetrahedron Lett.*, (1981) 959.

[86] E. Nakamura, Y. Miyachi, N. Koga and K. Morokuma, *J. Am. Chem. Soc.*, **114** (1992) 6686.

[87] F. Olbrich, J. Kopf and E. Weiss, *J. Organomet. Chem.*, **456** (1993) 293.

[88] F. Olbrich, G. Schmidt, E. Weiss and U. Behrens, *J. Organomet. Chem.*, **456** (1993) 299.

[89] J. Schwartz, *Tetrahedron Lett.*, (1972) 2803.

[90] T.L. Macdonald and W.C. Still, *J. Am. Chem. Soc.*, **97** (1975) 5280.